

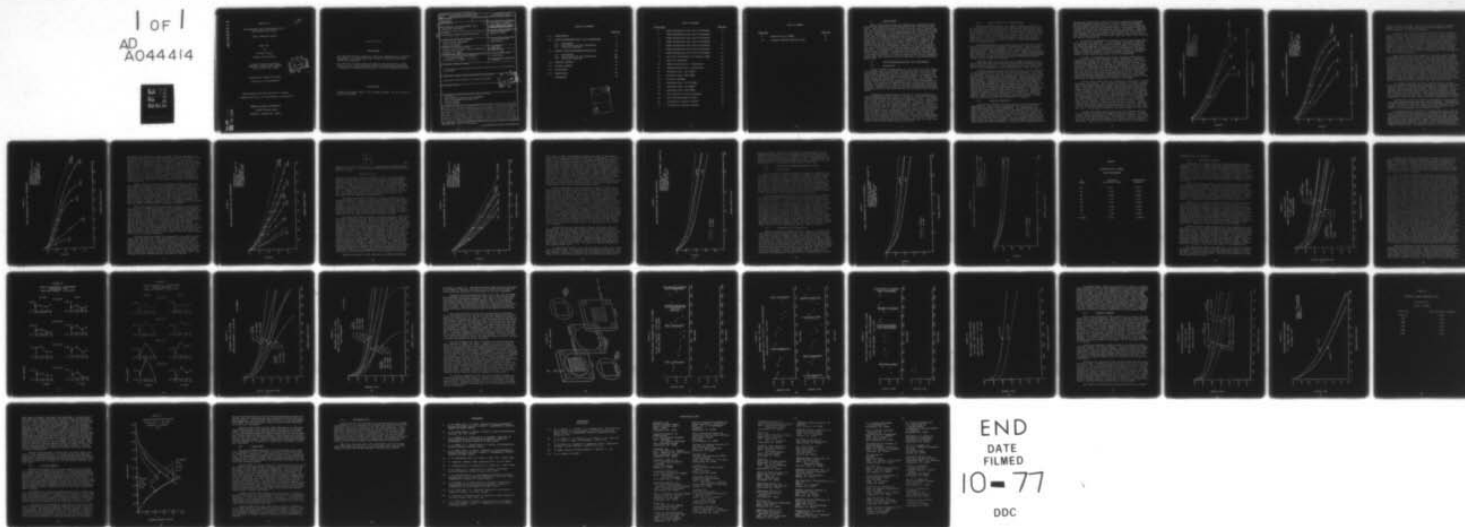
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NEW MATERIALS FOR FLUOROSULFONIC ACID
ELECTROLYTE FUEL CELLS

FINAL TECHNICAL REPORT

JUNE 1977

by

Michael George

Stanley Januszkiewicz

US ARMY MOBILITY EQUIPMENT
RESEARCH & DEVELOPMENT COMMAND
Fort Belvoir, VA 22060



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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Hydrogen-air fuel cells were evaluated with both TFMSA monohydrate and dilute TFMSA. Pressurized monohydrate cells were run at power levels comparable to phosphoric acid fuel cells under similar conditions. Fuel cells with from 25 to 60% TFMSA were evaluated at 25 and 70°C. A cell with 50% TFMSA was run for over 2,000 hours at room temperature without acid replenishment. Power densities in excess of 130mW/sq cm could be achieved at ambient temperatures and pressures with low loading catalysts. The evaluation of supported platinum and tungsten carbide catalyst with dilute TFMSA was initiated. Silicon carbide was investigated as a matrix material with TFMSA.		

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1. INTRODUCTION

This is the final report for Contract No. DAAK02-75-C-0045 entitled New Materials for Fluorosulfonic Acid Electrolyte Fuel Cells. The initial objective of this contract was to develop new fuel cell materials or adapt existing fuel cell components for use with the monohydrate of trifluoromethanesulfonic acid as the electrolyte. During the initial first half of this contract it was shown that the TFMSA monohydrate had certain volatility, wetting and conductivity characteristics which appeared to limit its application in a practical fuel cell. Subsequently, emphasis was placed upon the evaluation of aqueous solutions of TFMSA as an electrolyte for low temperature fuel cells. The change to the aqueous electrolyte considerably reduced much of the diffusional and ionic polarization losses associated with TFMSA monohydrate fuel cell. In conjunction with the aqueous TFMSA study, tungsten carbide was evaluated as a possible low temperature hydrogen oxidation electrocatalyst. Efforts were also directed at developing an inorganic type fuel cell matrix comprised of silicon carbide to insure long term stability with the corrosive trifluoromethanesulfonic acid.

2. TRIFLUOROMETHANESULFONIC ACID MONOHYDRATE

2.1 Background

Direct oxidation hydrocarbon air fuel cells utilizing common electrolytes such as phosphoric and sulfuric acid have been examined by many investigators over the past decade. Much of the research was centered on improving electrocatalysts to enhance the kinetics for the hydrocarbon oxidation reaction. The approach was never completely successful in a practical fuel cell as large losses occurred due to the slowness of the direct hydrocarbon reaction. In recent years emphasis has been placed upon the use of improved electrolytes to enhance the direct hydrocarbon oxidation reaction. Studies on the use of alternate electrolytes revealed a promising family of new electrolytes, the perfluoroalkane sulfonic acids.¹

Subsequent investigation of the use of the monohydrate of trifluoromethanesulfonic acid for the direct oxidation of propane showed considerable improvement over phosphoric acid.² The limiting current density for the propane oxidation in TFMSA monohydrate was a factor of 15 greater than for H_3PO_4 . Subsequent studies also indicated that the TFMSA monohydrate enhanced the electrooxidation of both pure and impure hydrogen as well as the electroreduction of air.^(3,4,5) The studies on the air electrode indicates that the open circuit potential utilizing TFMSA monohydrate was 150 mV closer to the thermodynamic reversible oxygen potential than was the potential using phosphoric acid. Enhanced performance was also noticed for the same air electrode in TFMSA monohydrate at all operating current densities. The studies involved smooth platinum electrodes rather than porous fuel cell type electrodes, thus current densities were very low.

2.2 Acid Properties and Preparation

Trifluoromethanesulfonic acid (TFMSA) commonly referred to as triflic acid or trimsylate acid (3M Company) can be described as a hygroscopic and stable liquid that shows resistance to thermal decomposition and hydrolysis.⁶ In addition, it has been shown to be the strongest monoprotic acid known.⁷ The boiling point of TFMSA is only 162°C which makes high temperature fuel cell use problematic. Mixture of the TFMSA with an equal molar amount of water can produce a less volatile product, trifluoromethanesulfonic acid monohydrate.

The TFMSA monohydrate evaluated under this contract was prepared by the method of Gramsted and Haszeldine.⁸ This technique utilizes successive distillations until a final product is collected at 217°C. The monohydrate was a white needle like crystalline mass with a melting point of 33 to 34°C. These distillations were conducted in all glass apparatus with polytetrafluoroethylene strips acting as boiling chips and polytrifluorochloroethylene grease to seal ground glass joints.

Available data on the volatility of TFMSA monohydrate suggests that acid loss from fuel cells operating at moderate temperatures should be minimal. It was determined that the vapor pressure of the monohydrate was only approximately 2 torr at 100°C.⁹

Trifluoromethanesulfonic acid was known to be very corrosive to all organic materials except for the fluorocarbons. A series of immersion tests at 121°C of various materials in the acid monohydrate also indicated that the monohydrate would severely attack organics such as polyethylene, polysulfone, and phenol-formaldehyde (Kynol). Fluorocarbons such as polytetrafluoroethylene and polyvinylidene fluoride showed no weight loss but were readily wetted by the monohydrate. This phenomena had previously been observed by Ackerman and Stuenkel when PTFE bonded fuel acid electrodes were flooded by the TFMSA monohydrate.¹⁰ Inorganic materials such as tantalum oxide and boron nitride were corrosion tested and appeared to be impervious to monohydrate. Although graphite composite structures tended to discolor the TFMSA monohydrate, there was little evidence of any major attack. Metals such as tantalum and gold also appeared to be stable.

2.3 Technical Approach

The general objective for this program was to develop new components or adapt existing components for use with the trifluoromethanesulfonic acid monohydrate. The monohydrate was viewed as a possible replacement for phosphoric acid for both direct and indirect hydrocarbon fuel cells operating at 135°C and above. Major emphasis was to be placed upon both electrode and matrix development during this phase. It was recognized that the electrode structure would present a major challenge since conventional acid fuel cell electrodes with PTFE binders would readily flood with the TFMSA monohydrate. Available for evaluation in the

monohydrate electrolyte at the outset were components developed for the phosphoric acid fuel cell. This included PTFE bonded platinum black electrodes and a variety of fuel cell matrices including Kynol, quartz, and tantalum oxide. Electrodes containing 5 mg/cm² Pt black were selected for initial evaluation. Higher Pt loadings of from 20 to 50 mg/cm² would probably be beneficial but were thought to be unrealistic at the time in view of the fact that phosphoric acid cells were being operated stably with loadings as low as .25 mg/cm² Pt.

No effort was expended in evaluating direct hydrocarbon fuel cells during this contract. It was thought necessary to develop an electrode structure that could be either made hydrophobic to the TFMSA monohydrate or could tolerate flooding to a certain degree. Since fuel cell performance of the monohydrate fuel cell would probably be controlled mainly by the relative gas diffusion rates to the air cathode, it was considered beneficial to limit losses at the anode by operating only on pure hydrogen.

In order to circumvent the obvious flooding tendencies of the relatively thin PTFE bonded Pt black electrodes, a pressure compensation system was utilized. The reactant gases; air at the cathode and hydrogen at the anode were pressurized in order to force electrolyte out of a portion of macropores of the electrode structure. Pressurization was obtained by simply placing a gage and valve on the exit line for each gas. By careful adjustment of the exit valve and gas regulators on the bottled gas supplies each side of the fuel cell could be pressurized to 30 psi. The pressure compensation approach although questionable for fuel cells operating for long durations was hoped to give some insight of the potential of TFMSA monohydrate with porous electrodes.

Initial cell builds with the monohydrate contained 6.5 square centimeter electrodes. The 5 mg/cm² Pt loaded - 25% PTFE catalyst layers were mounted on gold plated tantalum screen current collectors. Additional tantalum screens were placed behind both electrodes to serve as a gas diffusion path between the electrode and a flat tantalum plate serving as the cell housing. Viton gaskets were utilized to seal the cell. The pressurization technique was initially utilized with cells containing Kynol and quartz matrices at temperatures in the range of 107°C to 121°C. Cell instability was very evident as it was difficult to maintain an acceptable open circuit voltage. Attack of the matrix was suspect on both cases which resulted in cross leakage of the two gases. Another problem area noticed during these preliminary tests was the evolution of thick white fumes emanating from both gas exit lines from the cells. Electrolyte volatility was under suspect at this time.

During subsequent testing some cell polarization data was obtained when cell operating temperatures were reduced. Figures 1 and 2 show respectively the data obtained for hydrogen-air cells with Kynol and quartz matrices. The results in general were very poor but some correlation between cell performance and pressure was noted. Analysis of the cell data indicated a much higher cell

FIGURE 1

TFMSA MONOHYDRATE FUEL CELL PERFORMANCE

HYDROGEN AIR
ELECTRODES 5 mg/cm² PT BLACK
MATRIX KYNOL
TEMPERATURE 71°C
CELL RESISTANCE .90Ω
6.5 SQUARE CM. CELL

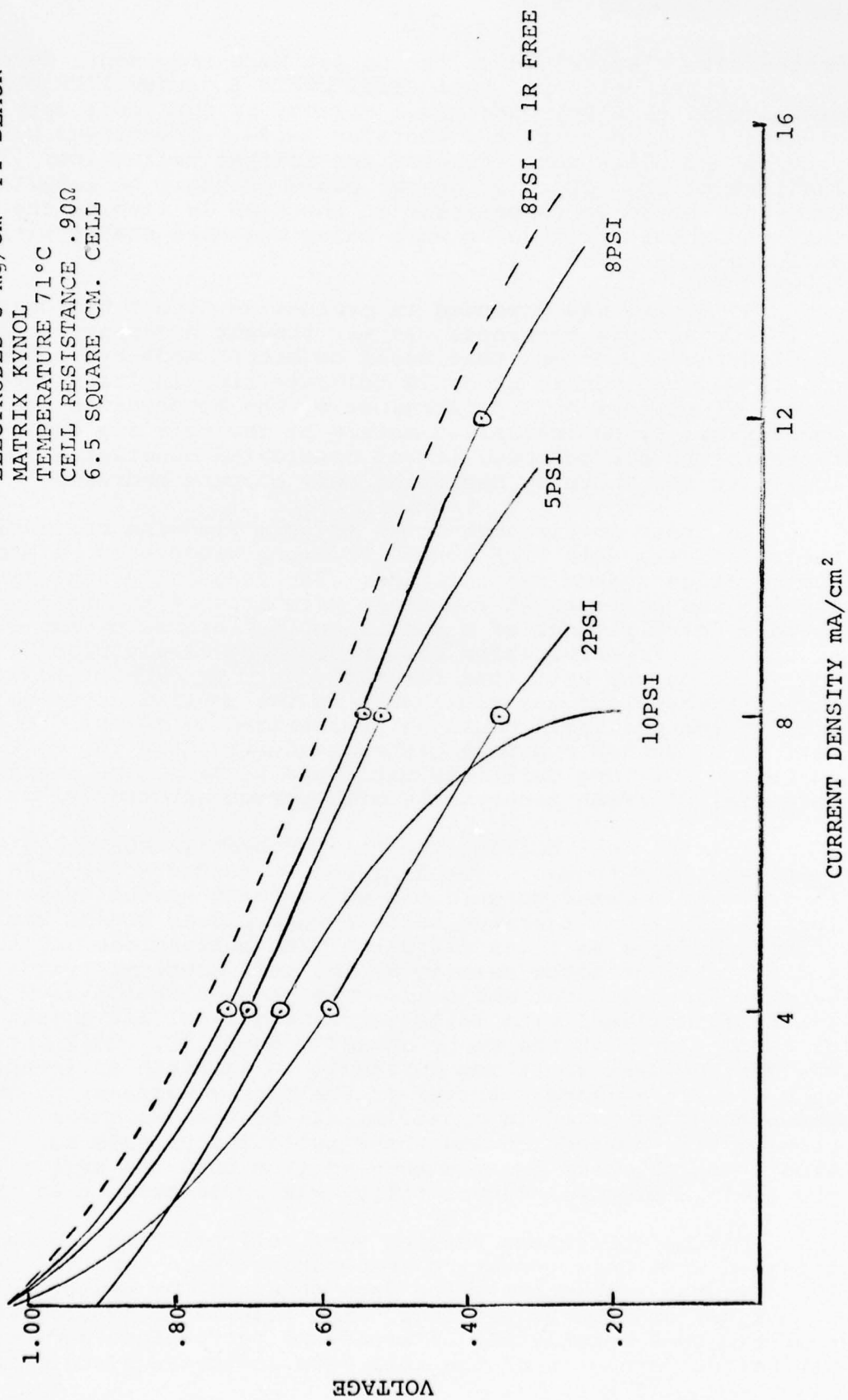
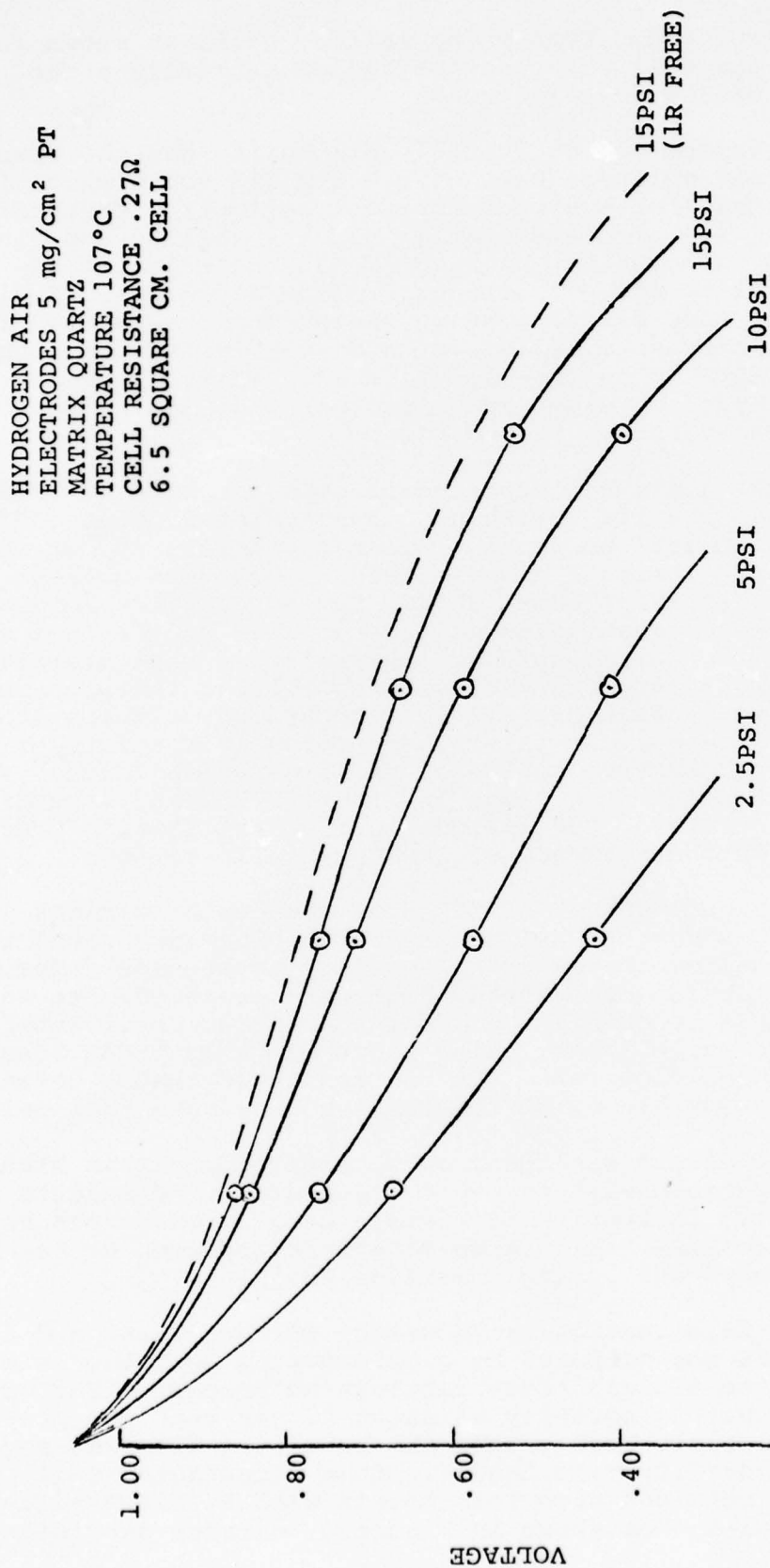


FIGURE 2

TFMSA MONOHYDRATE FUEL CELL PERFORMANCE



resistance than expected. Even on an IR free basis as shown in Figures 1 and 2, the cell polarization had an extremely steep slope indicative of flooded electrodes.

A positive aspect of the initial cell builds was the presence of open circuit voltages between 1.0 and 1.1 volts which is generally higher than for hydrogen-air fuel cells with phosphoric acid electrolyte. The problems with matrix instability and flooded electrodes was expected but unexpected was the evidence of electrolyte volatility and possible poor electrolyte conductivity. Subsequent efforts were directed at understanding the nature of fuming from the monohydrate cells. In addition, matrix development was emphasized. No obvious solution was available at the time of how to prepare an electrode structure that was hydrophobic with the TFMSA monohydrate.

Other investigators had reported no apparent loss of TFMSA monohydrate placed in a flask within an oven maintained at 135°C over durations of several weeks.¹¹ This was contrary to our observations in actual fuel cells where thick fumes were noticed in exit gas lines generally at about 90°C . Fuming occurred initially and usually in greater quantities at the air side of the fuel cell. It was originally thought that the monohydrate had been distilled improperly. Numerous attempts were made to improve the process including use of very clean distillation apparatus, elimination of grease about the ground glass joints, reduction in the rate of distillation and very selective choice of the final distillate. The product always distilled in a range of 216 to 217°C and crystallized at room temperature. Deviations in the distillation process had no influence on the tendency of the fuel cells to fume.

In another experiment at 120°C known amounts of various gases were bubbled through TFMSA monohydrate. When dry gases were utilized such as helium there was no tendency to produce fumes. However, when wet gases were passed, fogs were produced. It was concluded that TFMSA monohydrate vapor in the presence of water will produce thick white fumes. Also shown was that TFMSA loss was a function of gas flow rate. It was concluded that a definite temperature limitation did exist for TFMSA monohydrate fuel cells.

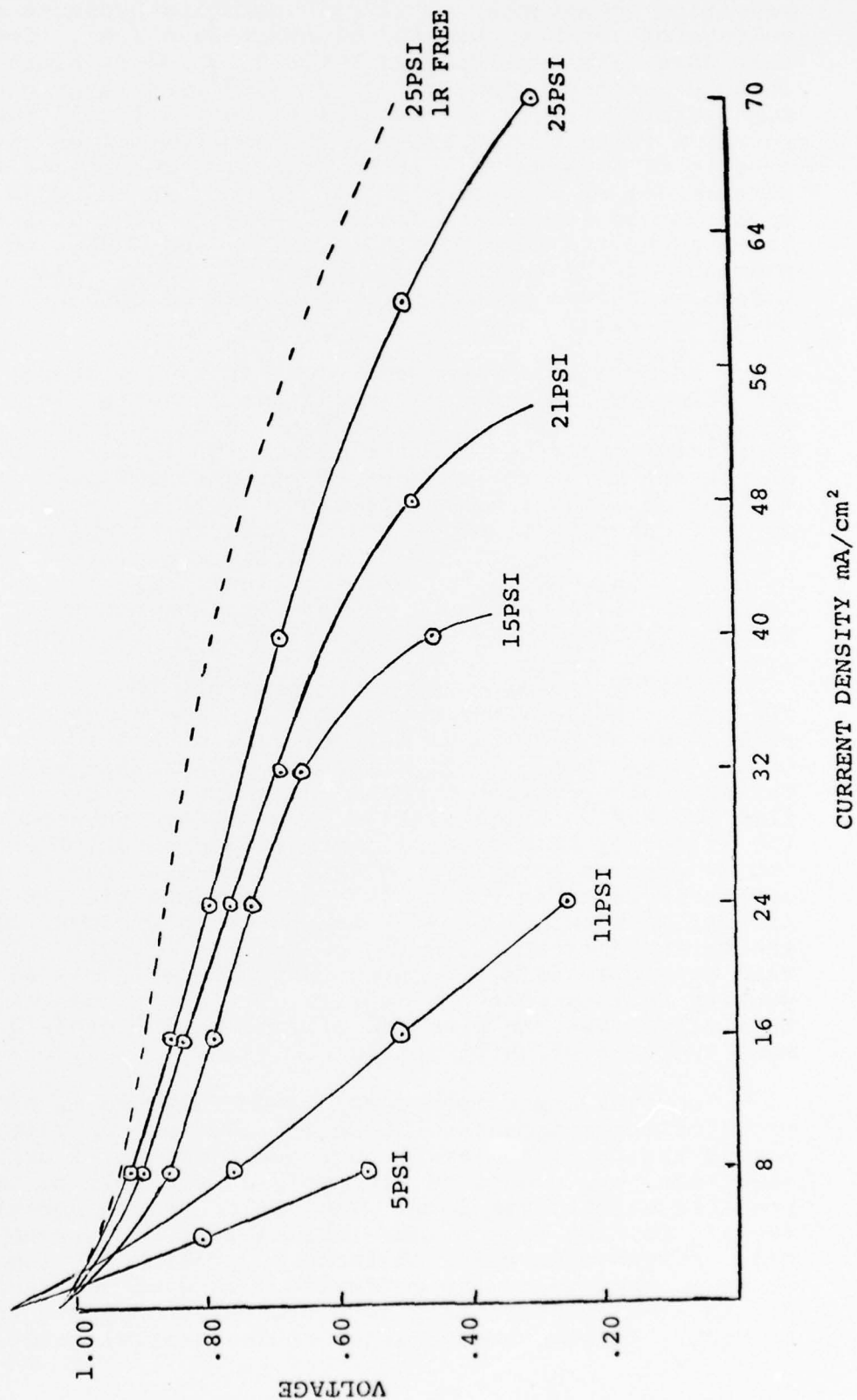
Considerable effort was spent on developing a matrix structure that was compatible with the acid monohydrate. Candidate materials included two inorganic materials, tantalum oxide and boron nitride, as well as PTFE. All three materials appeared to be stable in the monohydrate during immersion tests.

A composite film containing 75 weight percent Ta_2O_5 and 25 weight percent PTFE was prepared by a calendering operation similar in nature to the ERC electrode fabrication process. The experimental matrix with a porosity of about 41 per cent was prepared from a particulate Ta_2O_5 , thus the resulting film was somewhat nonrigid and difficult to handle. Some encouraging fuel cell performances were obtained with this matrix with Pt black electrodes in small cells. As shown in Figure 3, current densities of

FIGURE 3

TFMSA MONOHYDRATE FUEL CELL PERFORMANCE

HYDROGEN AIR
ELECTRODES 5 mg/cm² PT
MATRIX Ta₂O₅
TEMPERATURE 93°C
CELL RESISTANCE .45Ω
6.5 SQUARE CM. CELL



70 mA/cm² were obtained at high pressures with the pressure compensation technique. At 25 psi operating pressure an IR free cell voltage of .90 was obtained at about 16 mA/cm². Comparison of this data with published data for 5 mg/cm² Pt black air electrodes in 85 percent phosphoric acid at 120°C was favorable for the TFMSA monohydrate. Vogel and Lundquist from half cell measurements reported a value of .90 volts cathode potential on air at a current density of 5 mA/cm².¹² These promising results of the possible enhancement of the electroreduction of air in TFMSA monohydrate could not be duplicated however. Part of the difficulty was attributed to the poor physical quality and suspected low bubble pressure of the tantalum oxide matrix. Many cells exhibited gas crossover before meaningful data could be obtained in the pressurized fuel cell.

Boron nitride appeared to be initially attractive for use with TFMSA monohydrate as it was available in fibrous form. The very small fibers were believed to be capable of exerting good capillary attraction for the electrolyte. Composite structures of 50 percent boron nitride and 50 percent PTFE were prepared by a conventional paper making process. Matrices were obtained with porosities of 60 to 65 percent. Efforts to build cells with the boron nitride composite matrix were disappointing as current densities of only 40 mA/cm² were obtained. The matrix appeared to have nonuniform wetting behavior with the monohydrate and the boron nitride fibers lacked adequate structural integrity.

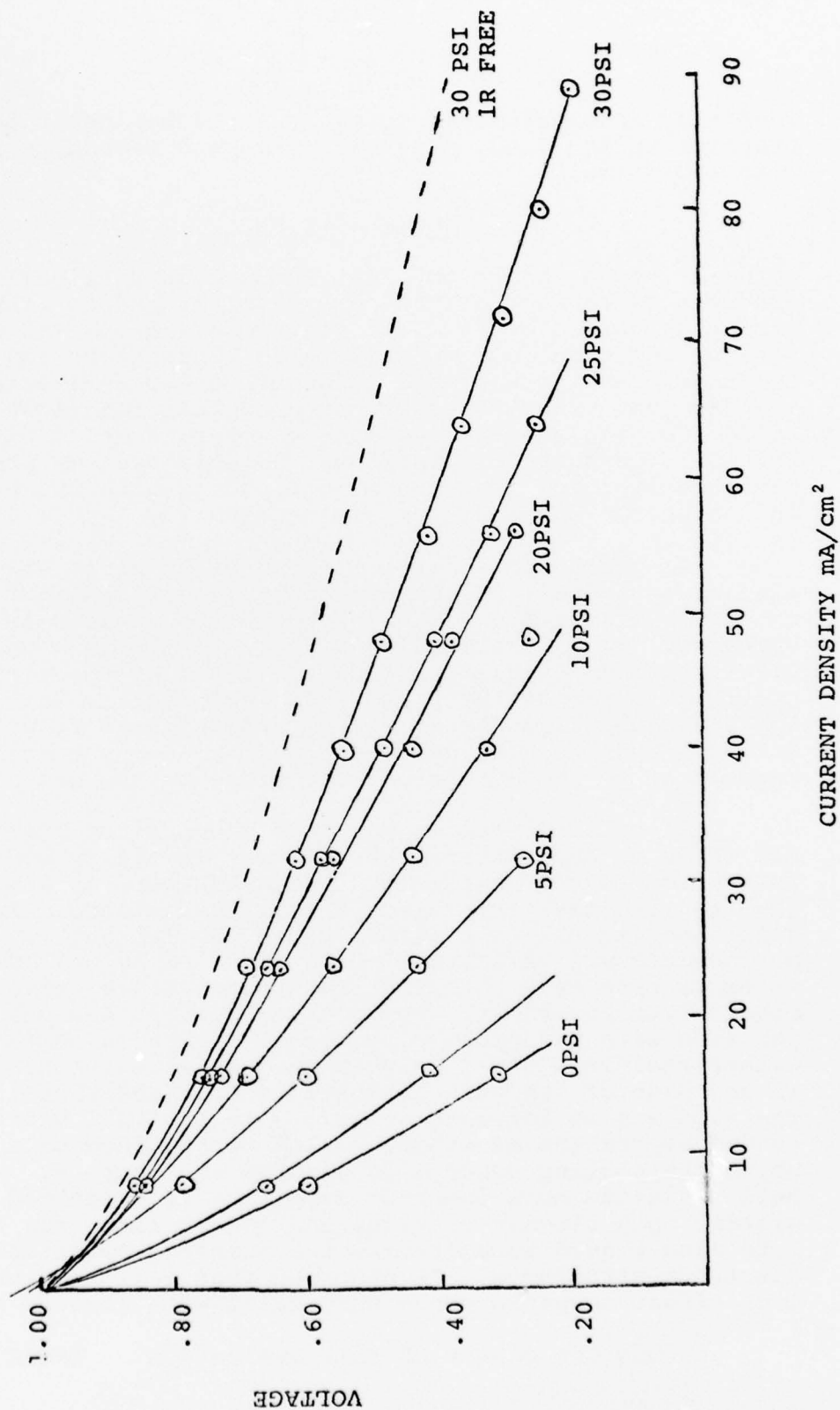
PTFE films appeared to be possibly the ideal matrix material for use with the TFMSA monohydrate. Some commercially available PTFE films of various porosities were evaluated and found difficult to uniformly wet. An experimental PTFE matrix was prepared by a calendaring operation from an admixture of a dry PTFE powder and a fine leachable filler such as zinc oxide. Subsequent removal of the filler by acid treatment produced a porous PTFE film approaching 70 percent porosity. A cell built with the experimental PTFE matrix is shown in Figure 4. Current densities approaching 100 mA/cm² were obtained at an operating pressure of 30 psi. Although the current producing capability of this cell was better than previous cells, the high performance levels at the low current density regions were not duplicated. A possible explanation for this effect was the presence of some slight cross gas leakage which made the cell slightly unstable.

Several other approaches were evaluated in an effort to improve cell performance. These included use of alternate binders within the catalyst layer, increasing of the Pt content of the electrode, and use of an electrolyte reservoir to compensate for possible electrolyte loss. The use of polyphosphazenes as an alternate to PTFE as a binder in fuel cell electrodes was investigated. Polyphosphazenes had shown in preliminary laboratory tests to be impervious to the corrosive nature of the TFMSA monohydrate and to show less tendency to wet with monohydrate than PTFE. The inorganic polymer phosphazenes of the general formula

FIGURE 4

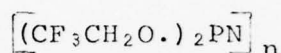
TFMSA MONOHYDRATE FUEL CELL PERFORMANCE

HYDROGEN AIR
ELECTRODES 5 mg/cm² PT
MATRIX PTFE
TEMPERATURE 88°C
CELL RESISTANCE .36Ω
6.5 SQUARE CM. CELL





generally in elastomeric form.¹³ A thermoplastic polyphosphazene prepared by the U. S. Army Materials and Mechanics Research Center with the formula



appeared to be easier to adapt for use in fuel cell electrodes. Attempts to fabricate fuel cell catalyst layers with the fluorinated phosphazene by standard electrode fabrication procedures were unsuccessful due to failure to bond the Pt and phosphazene together. Addition of small amounts of PTFE alleviated the bonding problem. Electrodes prepared by this technique were cured at 160°C. During several attempts to operate cells with 5 mg/cm² Pt - 35% phosphazene electrodes, no evidence was present to indicate any improved resistance to flooding with the new binder. This approach was subsequently terminated.

Increased noble metal loading of Pt black electrodes was also investigated. Electrodes containing 10 mg/cm² Pt were tested in PTFE matrix cells with no improvement noticed in overall cell voltages. It was rationalized that all platinum which is catalytically active by virtue of being wetted by the electrolyte is probably surrounded by pores which are equally wetted. If platinum black and PTFE have similar tendencies to be wetted by the acid monohydrate, the catalyst layer probably consists of flooded areas next to the matrix and dry areas on the gas side.

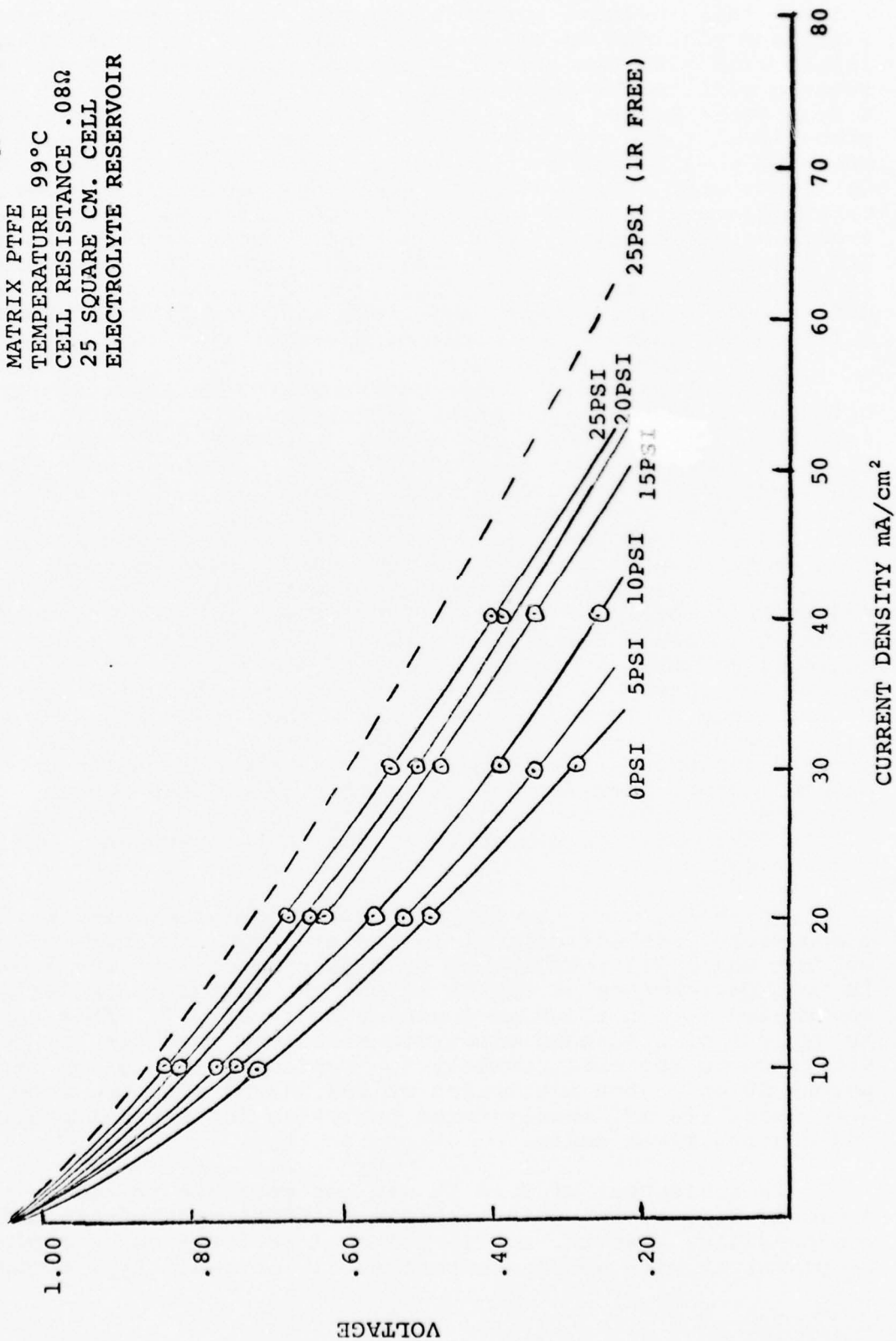
All cells described previously contained limited electrolyte. All TFMSA monohydrate in the cell was initially added to the matrix prior to cell assembly. The cells were marked with somewhat high and inconsistent values of cell resistance. In addition, the cells had limited life before cross gas leakage would occur. Cell performance was definitely being affected by cell dryout. Several attempts were made to build TFMSA monohydrate cells containing an electrolyte reservoir. The pooling concept was utilized in conjunction with 25 square centimeter electrodes contained within either stainless steel or graphite hardware. A slot was machined in one side of the cell hardware to hold additional electrolyte. The slot was in intimate contact with the cell matrix which extended beyond the electrodes. The performance of a typical cell using the pooling concept is plotted in Figure 5. Although the cell exhibited more inherent stability as evidenced by more consistent open circuit voltages and longer life, the excess electrolyte also tended to aggravate the flooding conditions within the electrode structures. It appeared that cell pressurization had less effect on performance than cells with limited electrolyte.

During the course of this evaluation of TFMSA monohydrate

FIGURE 5

TFMSA MONOHYDRATE FUEL CELL PERFORMANCE

HYDROGEN AIR
ELECTRODES 5 mg/cm² PT
MATRIX PTFE
TEMPERATURE 99°C
CELL RESISTANCE .08Ω
25 SQUARE CM. CELL
ELECTROLYTE RESERVOIR



fuel cells at ERC, considerable progress was made in developing supported catalyst type electrodes for use in phosphoric acid fuel cells. This included both use of platinum supported on carbon black and platinum doped Kocite electrodes.¹⁴ Supported catalyst layers with PTFE binders would also be susceptible to excessive wetting with the TFMSA monohydrate. Since the supported Pt was of a less dense nature in comparison to Pt black, it did appear more probably that a supported catalyst layer could be fabricated that would be more tolerant to flooding than Pt black layers. Supported catalysts were prepared by impregnating a commercially available carbon black with 10 weight percent of platinum. Fuel cell electrodes were fabricated with 50 weight percent PTFE by the standard ERC calendering process. A .040 inch thick layer containing 20 mg/cm² total catalyst loading (2 mg/cm² Pt) could be prepared by utilizing certain process deviations that resulted in essentially a less dense layer with increased macroporosity.

Initial attempts to operate supported catalyst electrodes with the pressure compensation technique and PTFE matrices led to some problems in wetting the active Pt within the catalyst layer. It was decided to test the experimental electrodes using more conventional test procedures. Kynol was again tried as a fuel cell matrix because it structurally was better than the experimental PTFE film. Kynol was judged acceptable with the monohydrate as long as temperatures were less than 90°C. Electrolyte was limited to only that necessary to saturate the matrix during cell assembly. Under these test conditions at 79°C it was possible to operate TFMSA monohydrate cells that were not drastically affected by diffusional losses. A typical performance curve for 25 cm² electrodes in graphite hardware is shown in Figure 6. The value for cell resistance of .050 ohms compares unfavorably to identically assembled cells containing phosphoric acid at 149°C (.020 ohms) and 50% TFMSA at 23°C (.016 ohms). Conductivity measurements of the monohydrate showed it to be considerably less conductive than aqueous TFMSA. Approximate values of .01 ohm⁻¹cm⁻¹, .23 ohm⁻¹cm⁻¹, and .40 ohm⁻¹cm⁻¹ were obtained respectively for the monohydrate, 50% TFMSA, and 20% TFMSA.

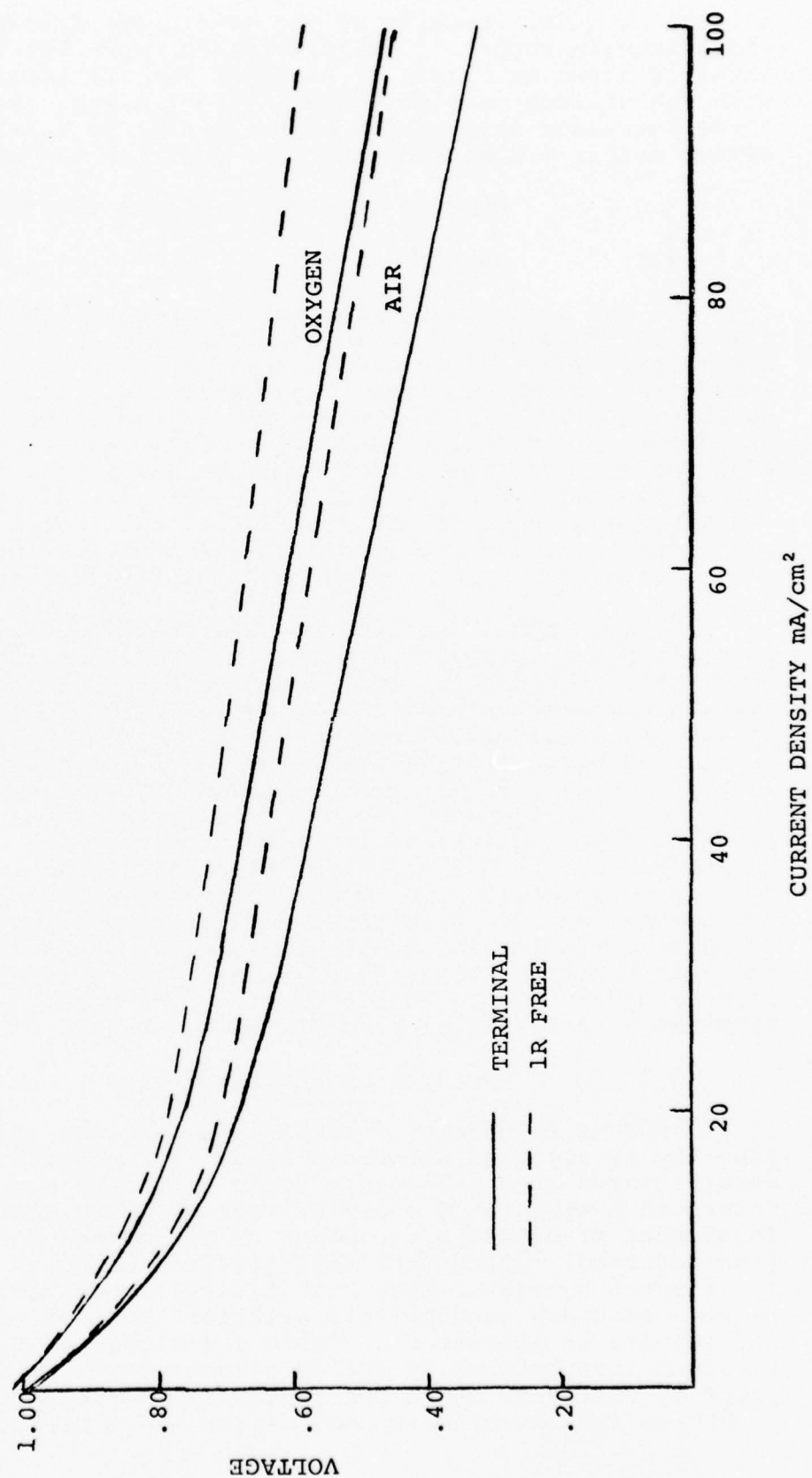
In addition to the large ohmic losses associated with the monohydrate, the diffusional losses as shown in Figure 6 become evident when cell performance is plotted on an IR free basis. The IR-free performance on oxygen beyond the activation polarization controlled region shows no tendency to level off. This behavior is typical of a flooded electrode structure resulting in poor gas diffusion to the electrocatalyst. Typical oxygen gains for the porous Pt on carbon electrodes at 100 mA/cm² with the monohydrate were about 140 mV, nearly twice the value for typical phosphoric and aqueous TFMSA cells.

In subsequent studies it was not possible to reduce the large ohmic or diffusional polarizations of TFMSA monohydrate cells. It was possible, however, to improve cell performance by replacing the Kynol matrix with another experimental inorganic type containing

FIGURE 6

TFMSA MONOHYDRATE FUEL CELL PERFORMANCE

ELECTRODES 10% PT/CARBON 2 mg/cm² PT
MATRIX KYNOL
TEMPERATURE 79°C
CELL RESISTANCE .05Ω
25 SQUARE CM. CELL



silicon carbide. Details of the matrix are described in a previous interim report.¹⁵ A performance curve for the improved level is shown in Figure 7. Reasons for the better performance with the silicon carbide matrix are not clear. Possibilities include increased utilization of the active Pt catalyst because of better matrix - electrode conformity within the cell.

3.0 AQUEOUS TRIFLUOROMETHANESULFONIC ACID

3.1 Background

At the approximate midpoint of this contract, work was initiated on evaluating aqueous solutions of TFMSA as electrolytes for matrix type fuel cells. A shift in emphasis from the TFMSA monohydrate to aqueous TFMSA was warranted. Even with the reduced volatility of the monohydrate in comparison to either the anhydrous acid or dilute acid, fuel cell operation above about 90°C was not possible without some signs of loss of electrolyte. In addition, it probably would be very difficult to maintain the electrolyte composition at exactly the azeotropic composition since matrix fuel cells have small electrolyte inventories which can be affected by water produced by cell operation.

Aqueous TFMSA appeared to be attractive because it eliminated the severe problem relating to the wettability of PTFE by the TFMSA monohydrate. It was also noticed during preliminary low temperature tests with aqueous TFMSA that electrolyte conductivity was considerably enhanced. A fuel cell performance curve using a 50 percent by volume solution of TFMSA in water is presented in Figure 8. It was concluded from these initial tests that electrode flooding was not occurring since oxygen gain values appeared to be equivalent to Pt black electrodes operating in phosphoric acid. A 2 mg/cm² Pt black electrode in phosphoric acid does typically give 80 mV difference between air and oxygen performance at 100 mA/cm² when not severely affected by flooding or other diffusional losses. The aqueous TFMSA tests were susceptible to cross gas leakage, thus limiting life, because of the poor integrity of the quartz matrix. The potential of the dilute TFMSA as a fuel cell electrolyte, however, had been shown.

3.2 Preparation and Properties

Aqueous solutions of TFMSA in water were prepared by diluting the as received anhydrous acid. For simplicity, solutions were prepared on a volumetric basis thus a 50 percent solution refers to a mixture of equal volumes of TFMSA and water. Significant heat of dilution did occur on mixing and some volume attrition occurred. Since fuel cell performance would be significantly affected by electrolyte resistivity, conductivity measurements using a standard conductivity cell were made of various dilutions. The results as presented in Table I indicate that maximum conductivity occurs between 20 and 30 percent TFMSA at 23°C. For a point of reference an 85 per cent TFMSA solution which is approaching the monohydrate composition had a conductivity of only

FIGURE 7

TFMSA MONOHYDRATE FUEL CELL PERFORMANCE

ELECTRODES 10% PT/CARBON 2 mg/cm² PT
MATRIX SILICON CARBIDE
TEMPERATURE 79°C
CELL RESISTANCE .05Ω
25 SQUARE CM. CELL

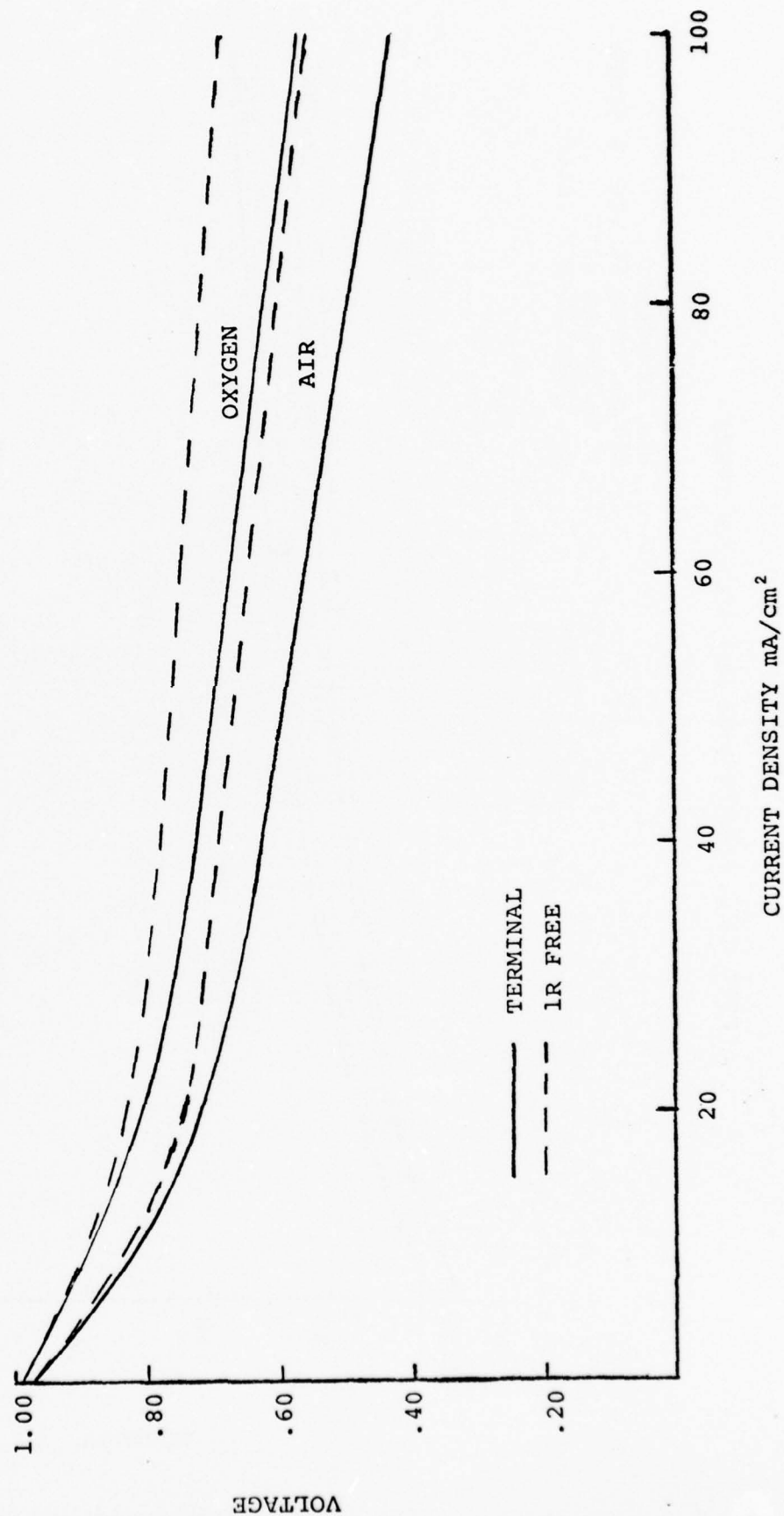


FIGURE 8

FUEL CELL PERFORMANCE FOR AQUEOUS TFMSA

ELECTRODES 2 mg/cm² PT BLACK
 MATRIX QUARTZ
 ELECTROLYTE 50 VOL. % TFMSA
 TEMPERATURE 23°C
 CELL RESISTANCE .016Ω

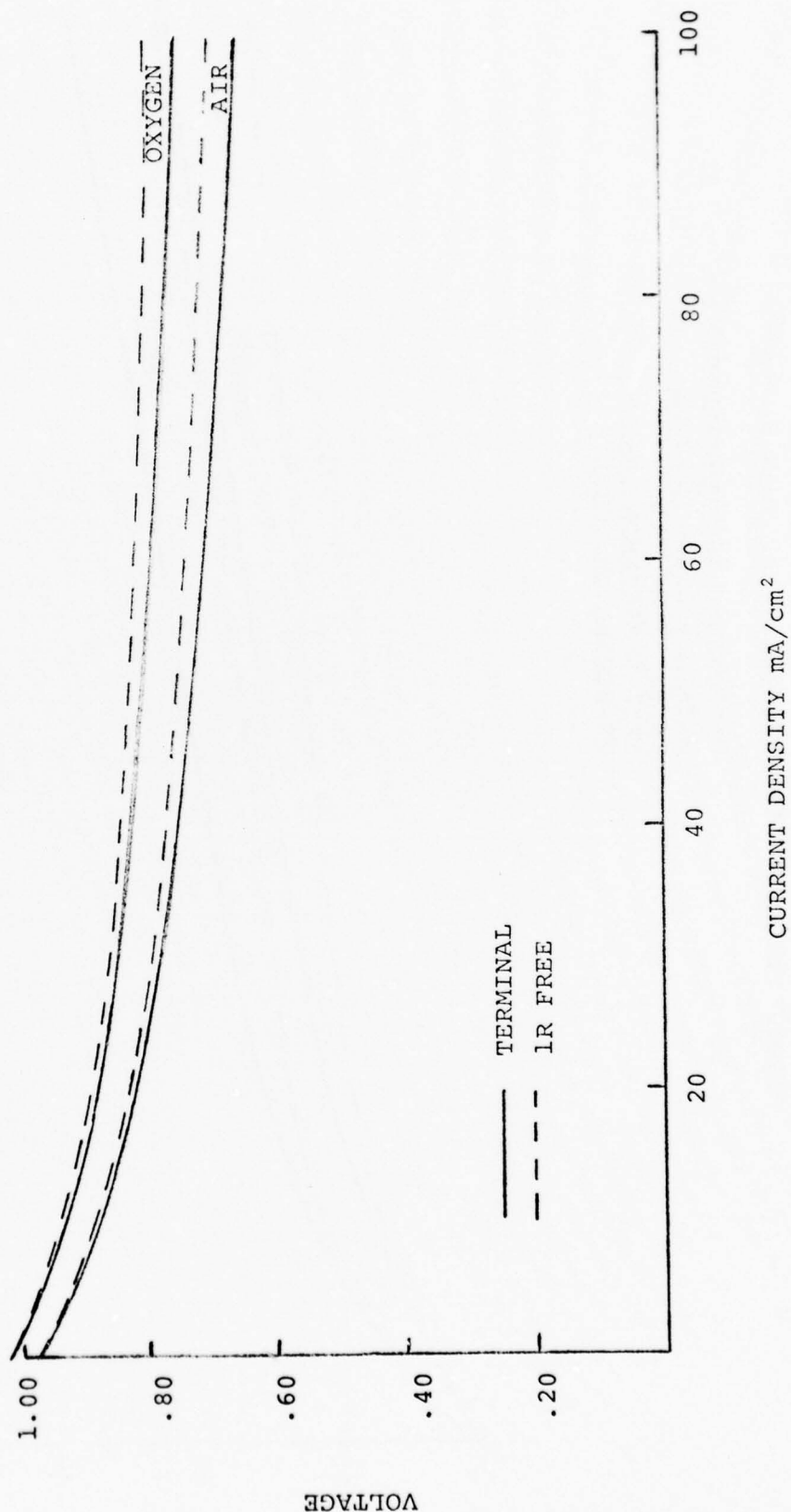


TABLE I

CONDUCTIVITY of TFMSA
ROOM TEMPERATURE

% TFMSA	Measured Resistance, Ohms	Conductivity mhos/cm
70	21.2	0.051
60	8.36	0.130
50	4.79	0.227
40	3.27	0.332
30	2.72	0.400
20	2.68	0.405
10	3.57	0.304
5	5.82	0.187
1N KCL	10.41	0.10439

approximately .01 mhos/cm.

3.3 Technical Approach

Evaluation of aqueous TFMSA fuel cells generally was conducted with fuel cell components and test techniques utilized in phosphoric acid fuel cells. This included use of 2 mg/cm² Pt black catalyst layers bonded with 25 percent PTFE and mounted upon a porous graphite paper substrate. Matrices evaluated included Kynol, glass fiber, and an experimental composite structure of silicon carbide and PTFE. Molded resin bonded graphite structures developed for phosphoric acid cells were judged acceptable for use as test plates to hold the 25 square centimeter electrodes to be evaluated.

Some differences, however, did exist between aqueous TFMSA and phosphoric acid cells. In particular, aqueous TFMSA cells were restricted to low temperatures generally in the range of 25 to 70°C while phosphoric acid cells can be operated at temperatures approaching 200°C. Another difference between the two electrolytes relates to the viscosity. Phosphoric acid being a relatively viscous liquid can actually aid in sealing cells. Dilute TFMSA has a much lower viscosity approaching that of water, thus there is a tendency for electrolyte to leak from test cells.

Emphasis was initially placed upon determining the optimum matrix structure for use with dilute TFMSA electrolyte cells. Candidate matrices included Kynol, Reeve Angel glass fiber paper, and an experimental composite structure developed under this contract consisting of a fibrous silicon carbide (Silag, Inc.) and PTFE. Some difficulty was initially experienced in starting cells at room temperature. It was suspected that some resistance to wetting of the active catalyst was occurring. This could be overcome by heating the cells overnight at 70°C with gases flowing. In some cases it was necessary to reverse the gas flow to the two electrodes within the cell to properly wet the hydrogen anode which had a tendency to wet slower than an air cathode.

Figure 9 shows a representative fuel cell performance curve for each of the three matrices operating on both hydrogen air and hydrogen-oxygen. The higher performance levels shown by the glass fiber and silicon carbide matrices is probably due to better matrix to electrode conformity within the cell. All three matrices had about the same thickness (.017 to .020") and attempts were made to compress each matrix to the same degree. Some slight differences in resistance was noticed for all three cells. An approximate value of .016 ohms, .013 ohms, and .012 ohms was determined for the Kynol, SiC, and glass fiber cells respectively.

The glass fiber matrix was selected to evaluate the effects of electrolyte composition and temperature upon initial cell performance. A series of cells were assembled containing 25, 37.5, 50, and 60 volume percent TFMSA. The cells were operated at both room temperature and 70°C.

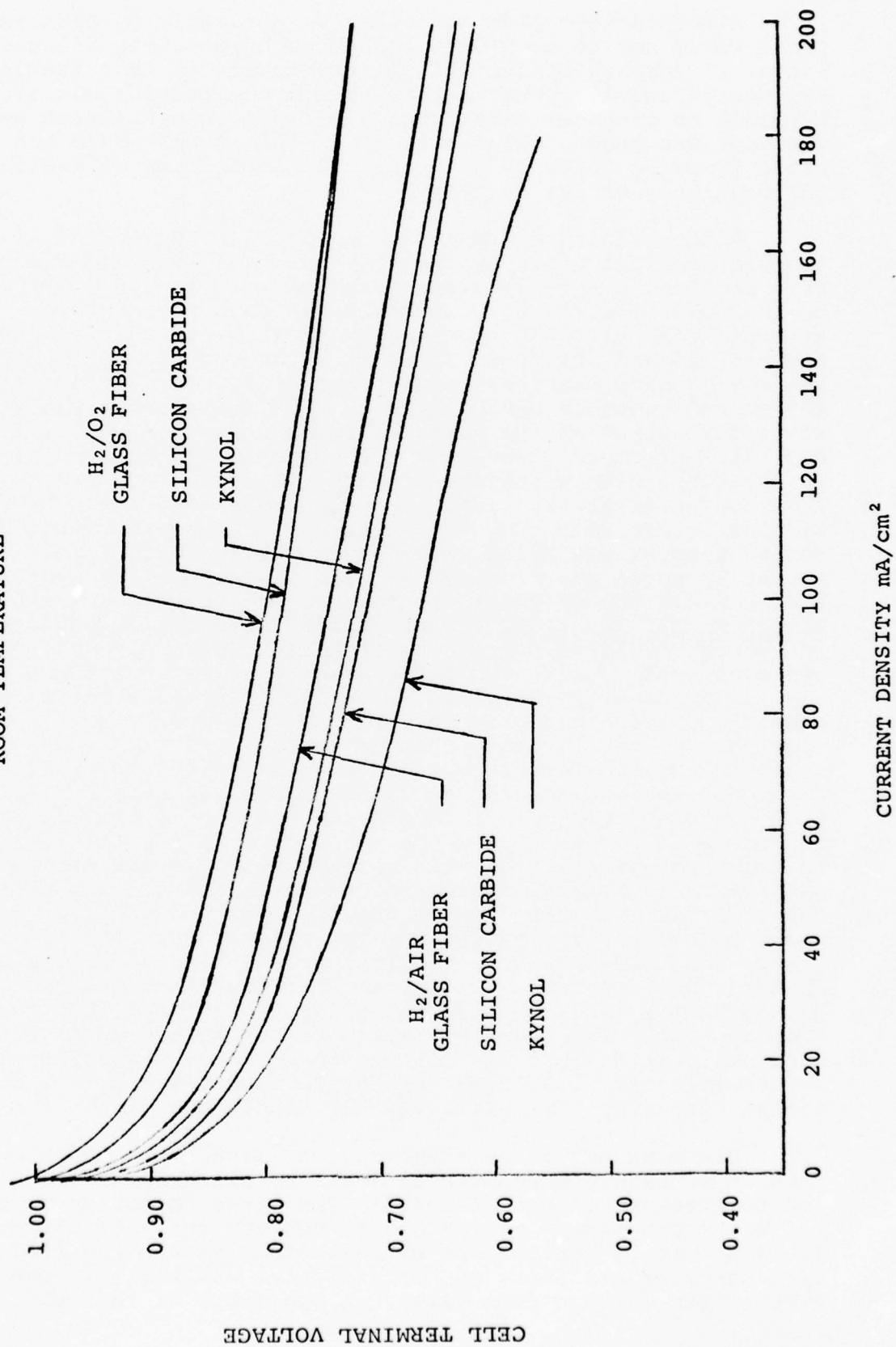
FIGURE 9

EFFECT OF MATRICES

ANODE AND CATHODE ~ 2 mg PT/CM²

50 VOL. % TFMSA

ROOM TEMPERATURE



Attempts were made to gather data rapidly so that test results would not be severely influenced by possible dilution affects. A summary of initial cell performances is presented in Figures 10 and 11. The best overall concentration was 37.5% although no clearcut relationship between concentration and performance was shown. Also evident at room temperature was a possible flooding tendency with the 60% electrolyte as indicated by the magnitude of the O_2 gains.

Although dilute TFMSA showed excellent potential as a low temperature fuel cell electrolyte, endurance testing did present some problems. Adequate water removal from continually operating cells would be difficult especially at room temperature. Initial attempts were directed at operating cells with initial concentrations of 25 and 50% TFMSA at 70°C. Hydrogen-air cells containing silicon carbide matrices were operated at a current density of 100 mA/cm². Stable performance at this temperature was not possible for either of the concentrations investigated. Initial decay rates of about .3 mV/hour were experienced for the first 125 to 200 hours with a subsequent higher decay rate approaching 1 mV/hour thereafter. Initial cell performance could be restored by flowing air over the cell anode. This suggested that some poisoning species was being oxidized at the anode surface. The effluent hydrogen gas from the anode did not smell of hydrogen sulfide nor did the effluent gas tend to precipitate an insoluble metallic sulfide. A similar test with sulfuric acid did result in hydrogen sulfide being formed as a reduction product at the hydrogen anode. Although the stability of aqueous TFMSA at 70°C was in question, it appeared to be a different mechanism than commonly experienced with sulfuric acid electrolytes. Other investigators have recently postulated the formation of sulfur from aqueous TFMSA at temperatures in excess of 60°C.¹⁶ Similar cells described above were also endurance tested at essentially room temperature. Cell performance as a function of time is presented in Figure 12 for the 25% TFMSA and Figure 13 for the 50% TFMSA. In order to operate the cells continuously, it was necessary to make daily additions of electrolyte to a reservoir in contact with the cell matrix. Air flow to the cell was about at the six stoichiometric rate, thus the water removal from the cell was generally insufficient. The electrolyte did tend to dilute and leak from the bottom of the cell around the gasketing material. Approximate lifetimes of 1100 hours for the 25% and 2500 hours for the 50% electrolyte were exhibited before severe decay occurred. Eventual cell failure was not due to an anode poisoning effect as was experienced at 70°C but appeared to be related to a diffusion effect caused by the relatively wet conditions within the cell.

Since an endurance capability of 2500 hours had been shown, aqueous TFMSA did appear to be a viable electrolyte for use in low temperature acid fuel cells. The water rejection problem from cells did complicate evaluation of the various cell components. In an effort to control the water balance within the cell, special cell hardware utilizing an "O" ring seal was built to prevent electrolyte leakage from cells. A schematic of the cell hardware

FIGURE 10

TFMSA CONCENTRATION - PERFORMANCE
 TEMPERATURE 70°C
 ANODE AND CATHODE - 2 mg PT/CM²

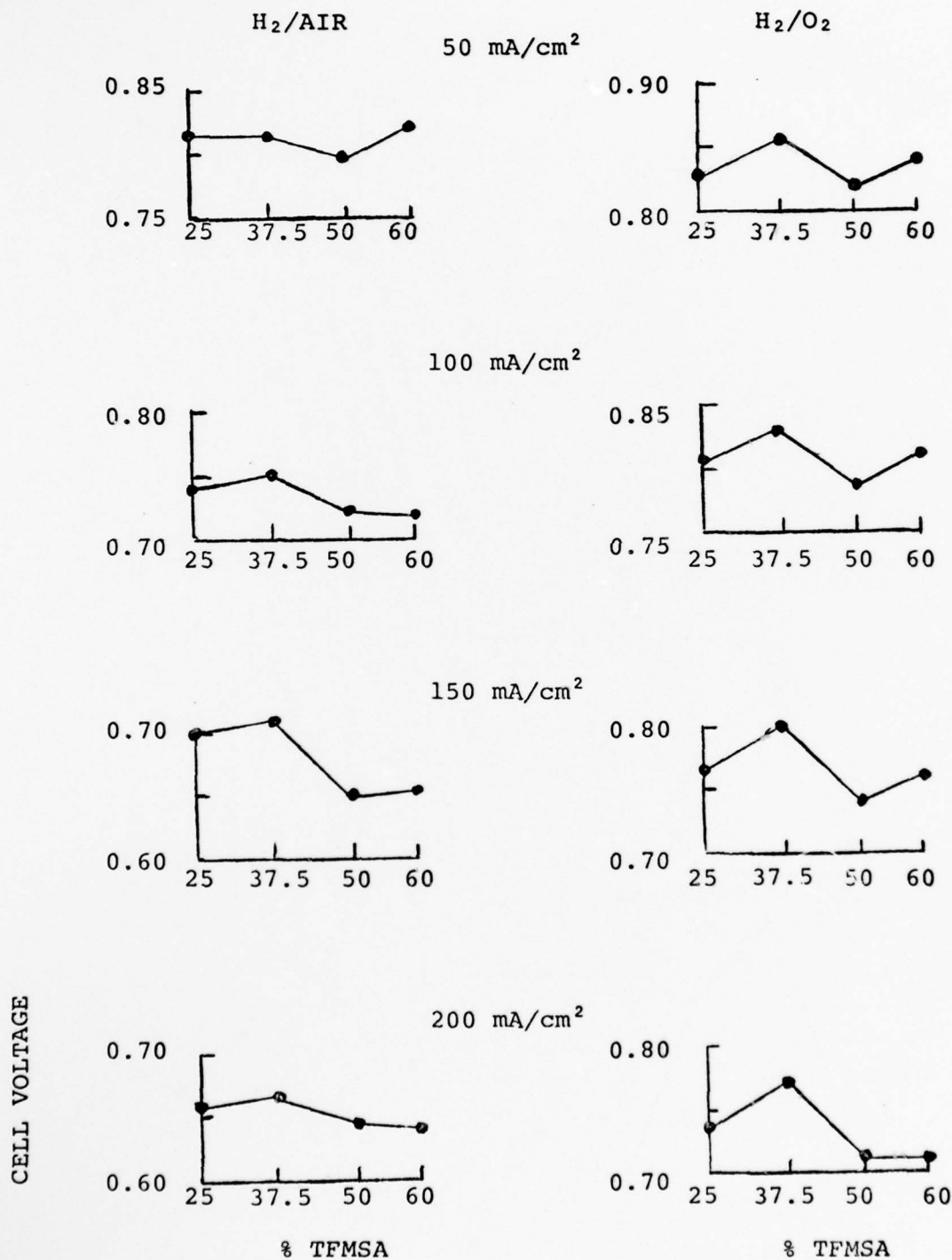


FIGURE 11

TFMSA CONCENTRATION - PERFORMANCE
ROOM TEMPERATURE
ANODE AND CATHODE - 2 mg PT/CM²

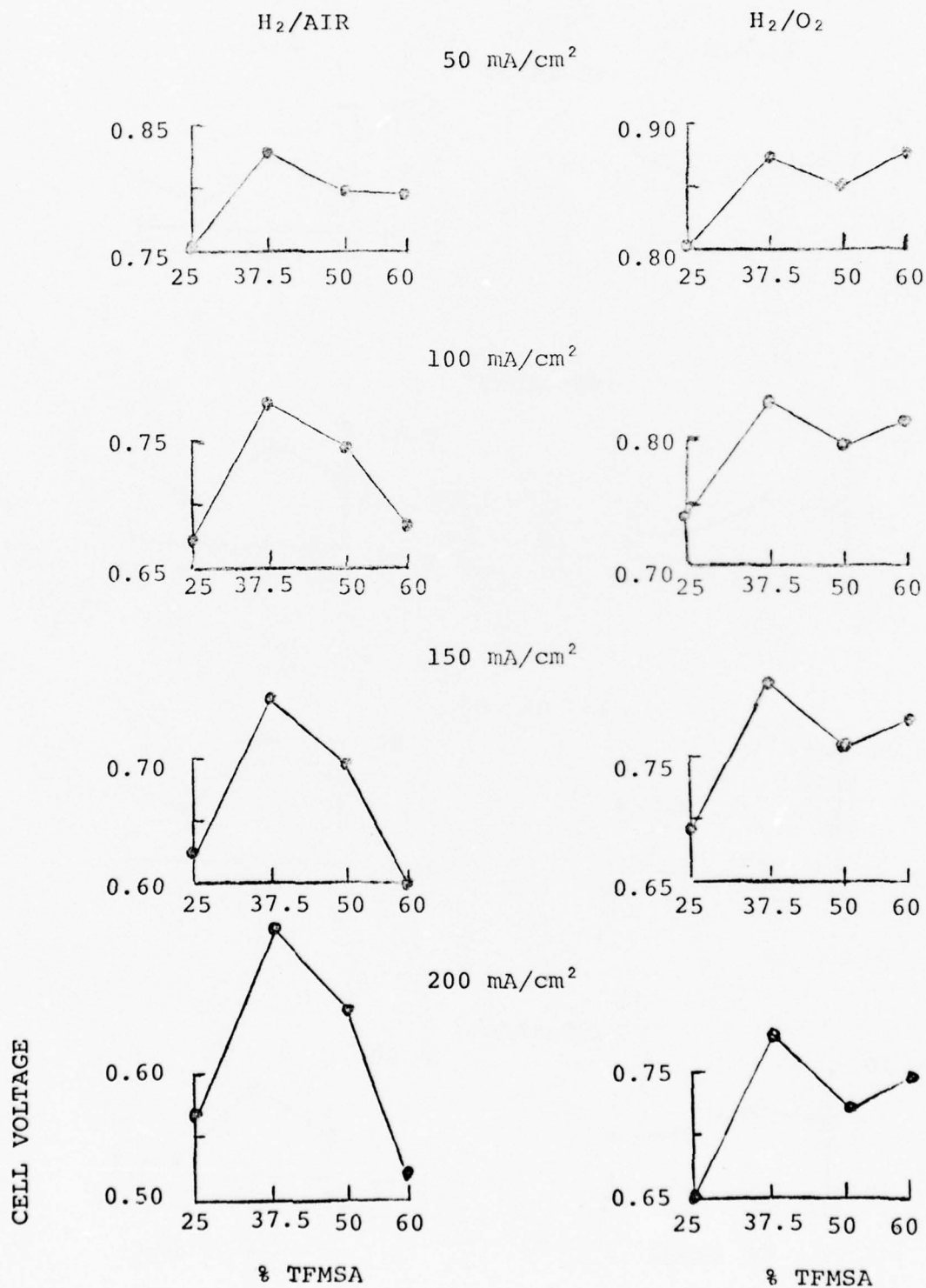


FIGURE 12

ENDURANCE TEST, 25% TFMSA

ANODE AND CATHODE - 2 mg PT/CM²

SiC MATRIX

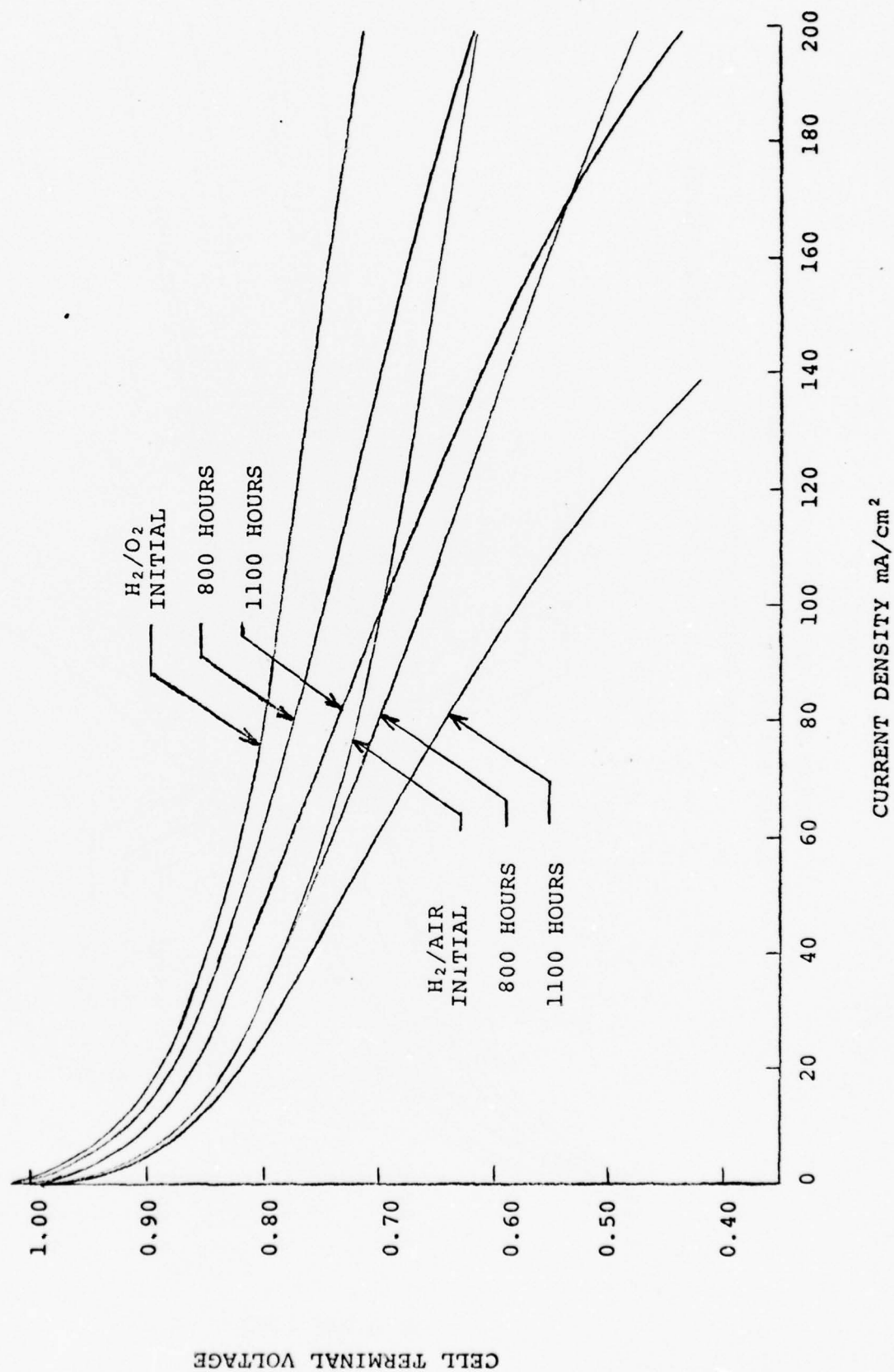
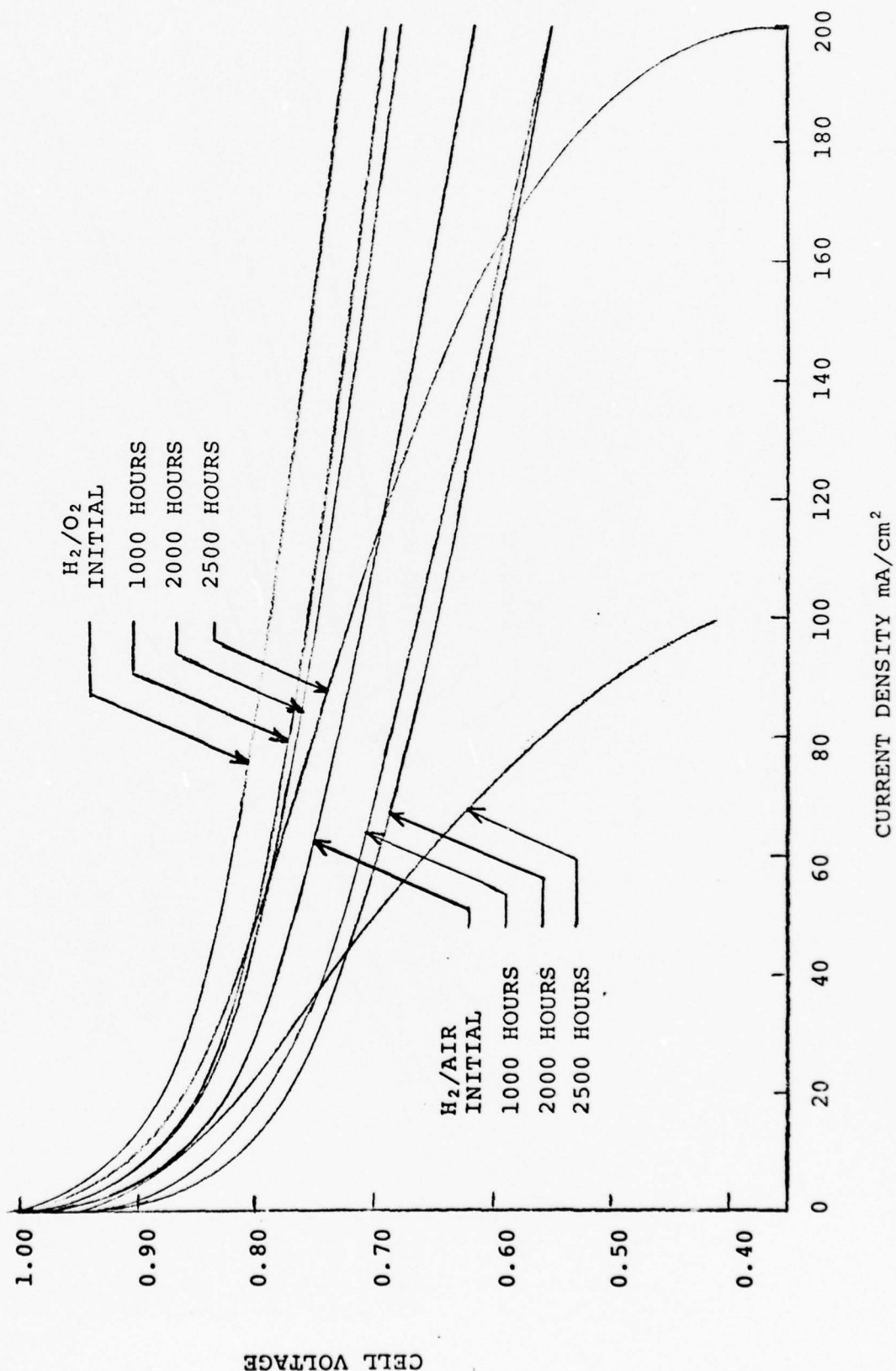


FIGURE 13

ENDURANCE TEST, 50% TFMSA
ANODE AND CATHODE - 2 mg PT/CM²
ROOM TEMPERATURE

SiC MATRIX



is shown in Figure 14. The design allowed some excess electrolyte to be added to the cell initially but no provisions were made to allow continual addition of electrolyte as the cell operated.

A series of cells containing 25%, 37.5%, 50%, and 60% TFMSA were assembled with glass fiber matrices and Pt black electrodes utilizing the new design hardware. Air flows to the cells were increased to about the 25 stoichiometric rate to remove water. Difficulties were encountered in operating the 25% electrolyte cells for more than several hours due to a tendency for gas cross-over to occur. The difficulty is believed associated with the poor electrolyte retention properties of the matrix with the 25% acid.

The endurance data for the more concentrated electrolyte cells operating on air at 100 mA/cm^2 and room temperature are presented in Figures 15, 16, and 17. During the course of testing absolutely no changes were made in the operating conditions of the cell unless noted in the endurance plot. No electrolyte was ever added to the cell nor was the load ever removed from the cell unless performance test was indicated. In most cases when the cell was allowed to operate continually under load a gradual loss of performance did occur. Initial performance could be restored however, by merely running a polarization test on both air and oxygen. A possible explanation for this phenomena might be related to the very high flow rates to the air cathode. A drying out effect could be occurring within the cathode structure which results in under utilization of the Pt catalyst.

The 37.5% TFMSA cell shown in Figure 15 did develop cross over problems at about 700 hours. Reduction of the air flow to about the 15 stoichiometric rate helped eliminate this tendency. Figure 16 shows that for a 50% TFMSA electrolyte fuel cell, an endurance capability of 2000 hours was demonstrated without the necessity of periodic electrolyte replenishment. All cell decay was of a reversible nature, probably related to percentage of catalyst utilization. Figure 17 for the 60% concentration shows a tendency for performance to improve with time. Initial performance was generally lower than for the more dilute concentrations indicating that diffusional and ionic resistance losses could have been greater. As the cell was operated, however, further dilution of the electrolyte probably was occurring. A noticeable drop in the cathode oxygen gain of 100 mV was noted between initial startup and 600 hours. A change in the wetting characteristics of the aqueous TFMSA upon PTFE could have been occurring. The cell performance at the 600 hour point is presented in Figure 18.

It must be pointed out that the cell terminal voltages exhibited by aqueous TFMSA cells at ambient temperatures were not as inherently stable as phosphoric acid cells operating at high temperatures. Fluctuations did occur on a daily basis, possibly due to slight changes in temperature or different degrees of catalyst utilization.

FIGURE 14
NEW CELL HARDWARE

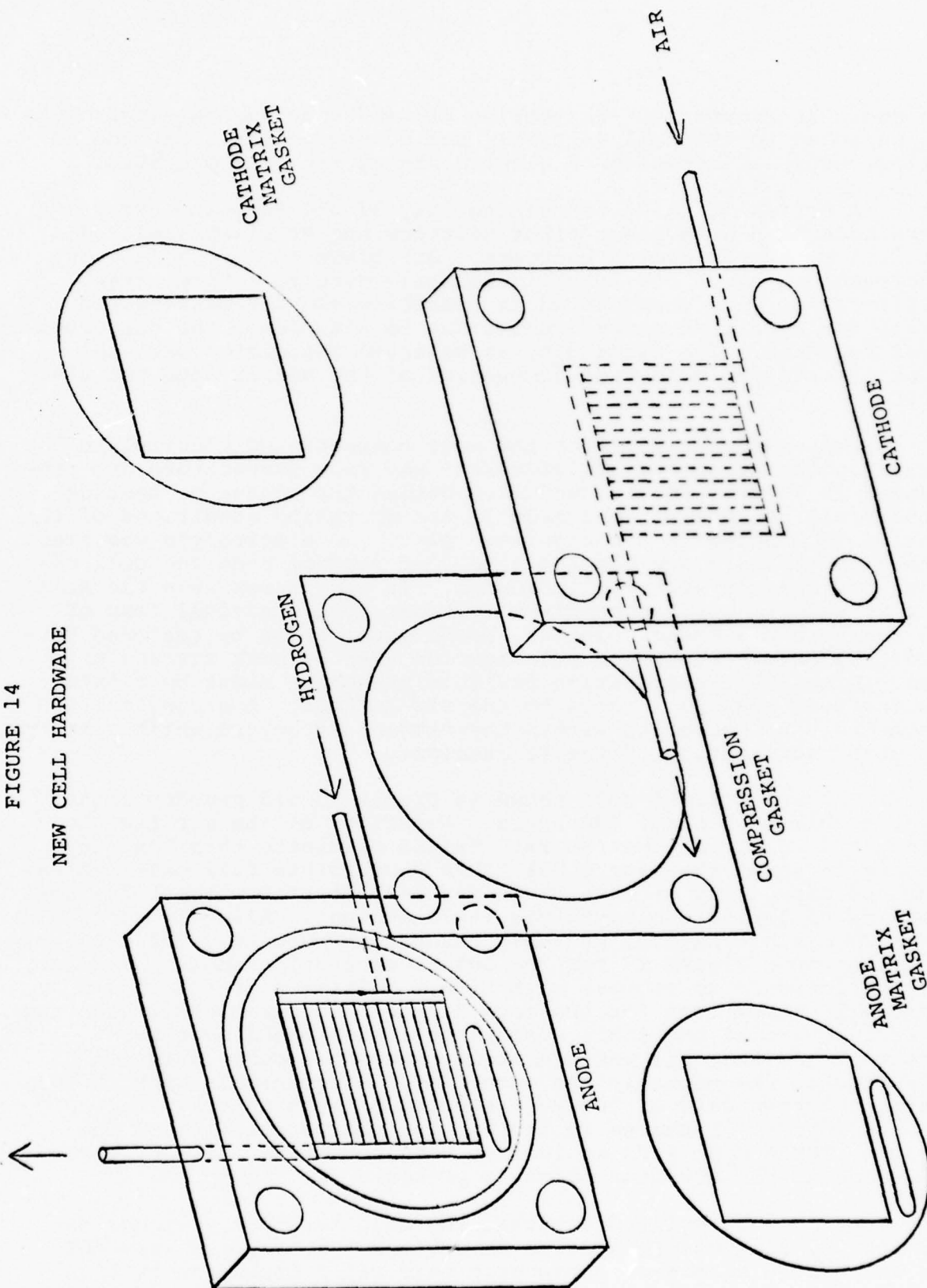


FIGURE 15

GLASS FIBER MATRIX ENDURANCE TEST, 37.5% TFMSA

H₂/AIR - 100 mA/cm² - ROOM TEMP.

ANODE AND CATHODE - 2 mg PT/CM²

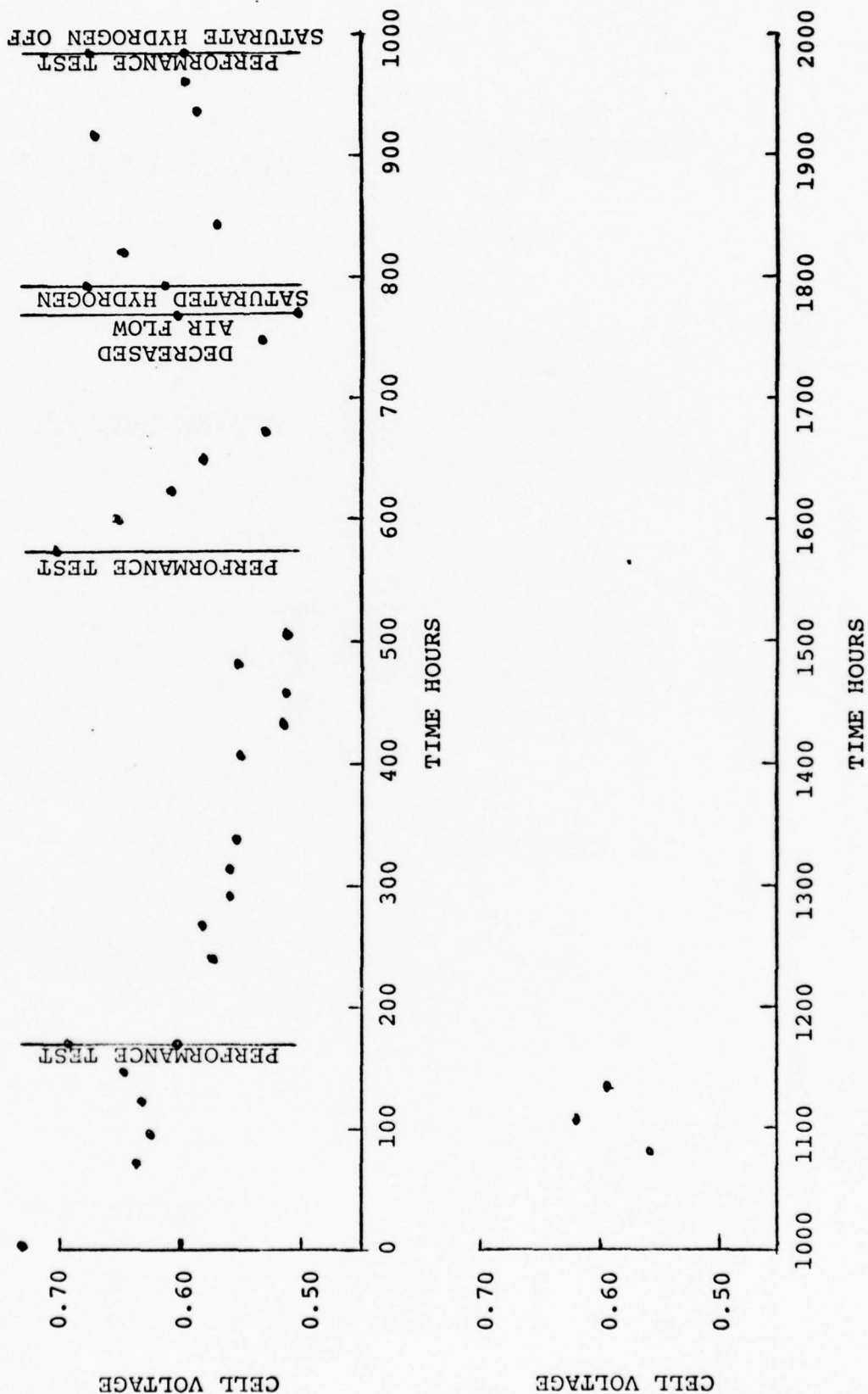


FIGURE 16

ENDURANCE TEST, 50% TFMSA

GLASS FIBER MATRIX H_2 /AIR - 100 mA/cm² - ROOM TEMPERATURE

ANODE AND CATHODE ~ 2 mg PT/CM²

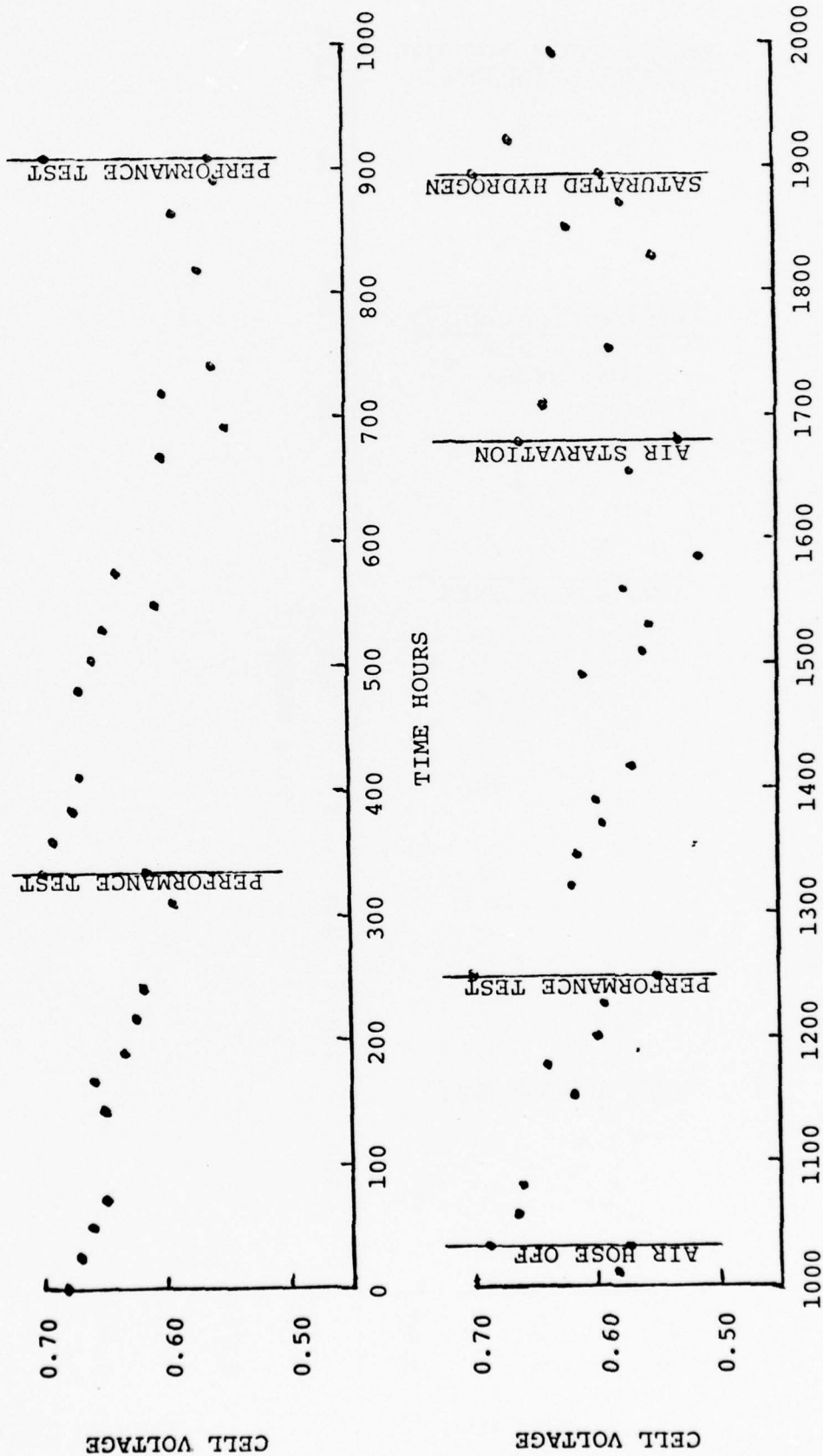


FIGURE 17

GLASS FIBER MATRIX ENDURANCE TEST, 60 TFMSA

$H_2/AIR - 100 \text{ mA/cm}^2 - \text{ROOM TEMPERATURE}$

ANODE AND CATHODE - 2 mg PT/ CM^2

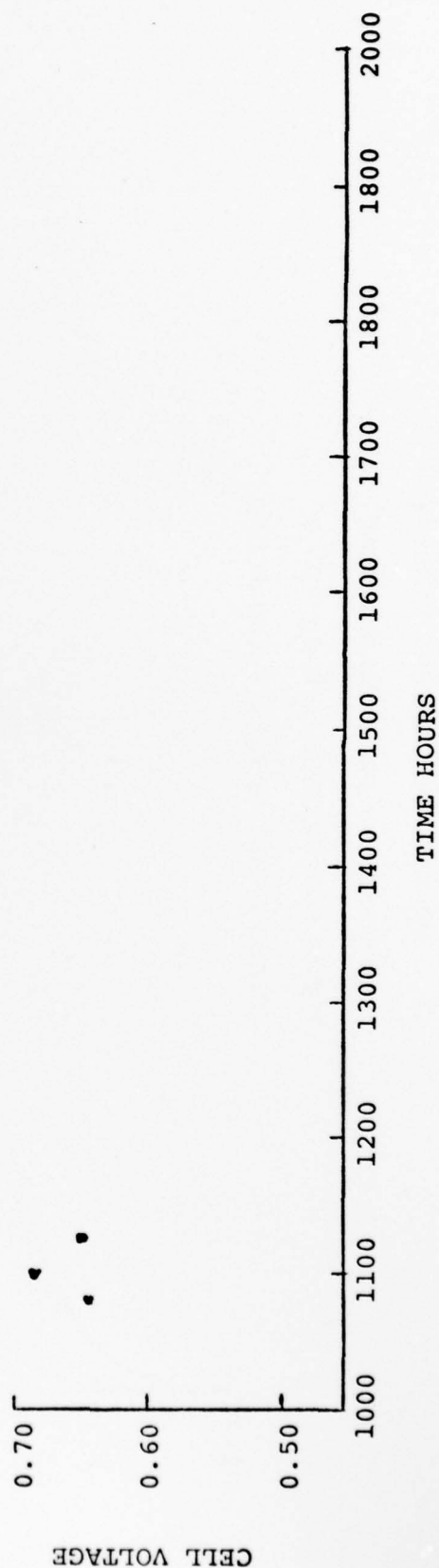
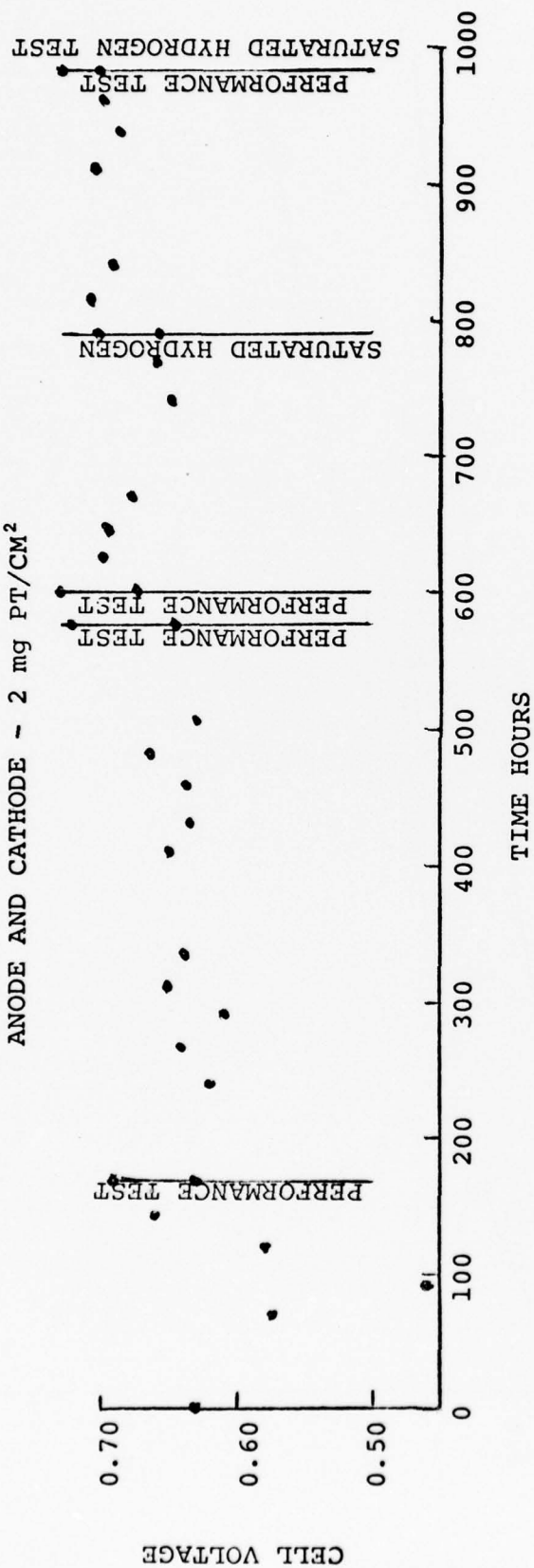


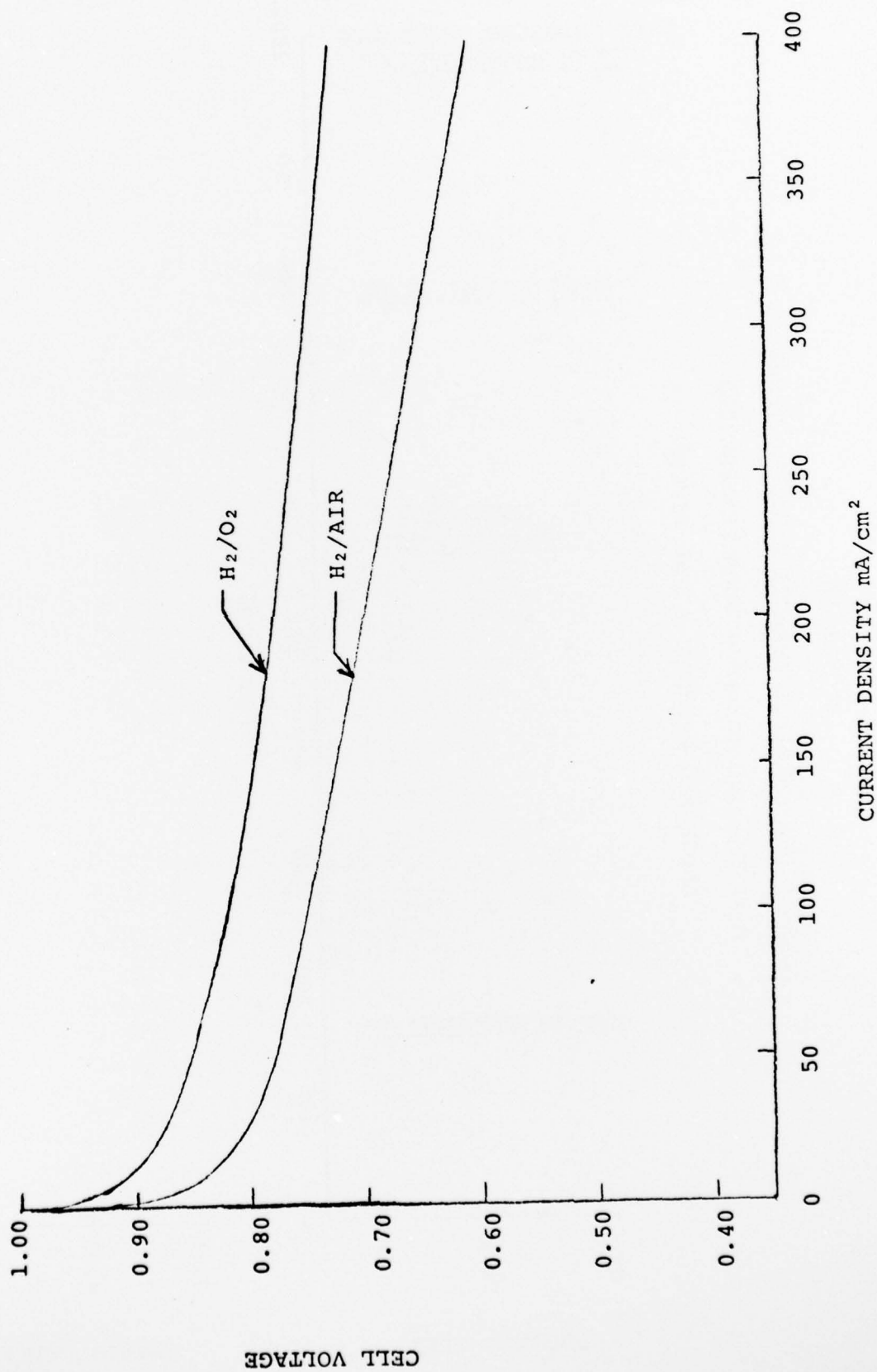
FIGURE 18

CELL VOLTAGE VS CURRENT DENSITY

60% TFMSA - ROOM TEMPERATURE

ANODE AND CATHODE - 2 mg PT/CM²

GLASS FIBER MATRIX - 600 HOURS



A limited effort during this contract was spent on evaluating supported catalyst type cathodes in conjunction with aqueous TFMSA electrolytes. The electrodes were prepared from a 10% Pt on carbon black catalyst and contained 50 weight percent PTFE. Figure 19 shows polarization results from several cell builds with various supported catalyst cathodes tested versus Pt black anodes with both Kynol and glass fiber matrices. The initial results as shown tend to indicate some diffusion problems with supported catalyst cathodes. Rapid decay believed to be the result of flooding generally occurred during endurance testing. Stability was improved by increasing electrode PTFE content to 60 percent but clearly more work is necessary to optimize a supported catalyst electrode structure compatible with the aqueous TFMSA.

4.0 TUNGSTEN CARBIDE

One of the purposes of this program was to explore the possibilities of using tungsten carbide as a hydrogen oxidation catalyst with aqueous TFMSA fuel cells. The investigation of tungsten carbide was believed warranted because other catalysts such as Pt black or noble metal alloys are severely poisoned by carbon monoxide especially at the low temperatures of interest under this program. A fuel cell grade tungsten carbide (Ultramicon) prepared by H. C. Starck with a nominal surface area of 8 sq meter per gram was the primary catalyst evaluated. Catalyst layers were prepared by a calendering process utilizing (10-15%) PTFE as a binder. For catalyst loadings of 80 mg/cm² WC or less, it was possible to utilize graphite paper as a substrate. An expanded tantalum screen was used as the support for WC loadings in excess of 80 mg/cm².

Testing of tungsten carbide anodes was conducted versus standard 2 mg/cm² Pt black cathodes. Cell evaluation was conducted with pooling type molded graphite hardware containing 25 cm² electrodes. Silicon carbide and glass fiber matrices were utilized to evaluate the experimental anodes since there appeared to be a basic incompatibility between WC and Kynol matrices. WC evaluation in aqueous TFMSA cells was restricted to the 50% concentration.

Startup of WC anode cells with aqueous TFMSA proved to be a difficult task. Indications were that the WC had to be initially activated. Activation procedures have been described in the literature for WC catalysts for use in sulfuric acid.^{17,18} It was possible to activate a 150 mg/cm² loaded Starck WC-15% PTFE electrode after several weeks within the cell. Activation was accomplished by periodic exposure of the anode to flowing air. Figure 20 shows the maximum performance levels obtained for the experimental hydrogen anode as tested with a standard Pt cathode and a silicon carbide matrix. A life test of this cell as presented in Table 2 indicated limited stability for the WC anode.

The insitu activation was considered tedious and attempts

FIGURE 19

10% PLATINUM/CARBON CATHODE

2 mg PT/CM² ANODE

50% TFMSA - ROOM TEMPERATURE

GLASS FIBER MATRIX

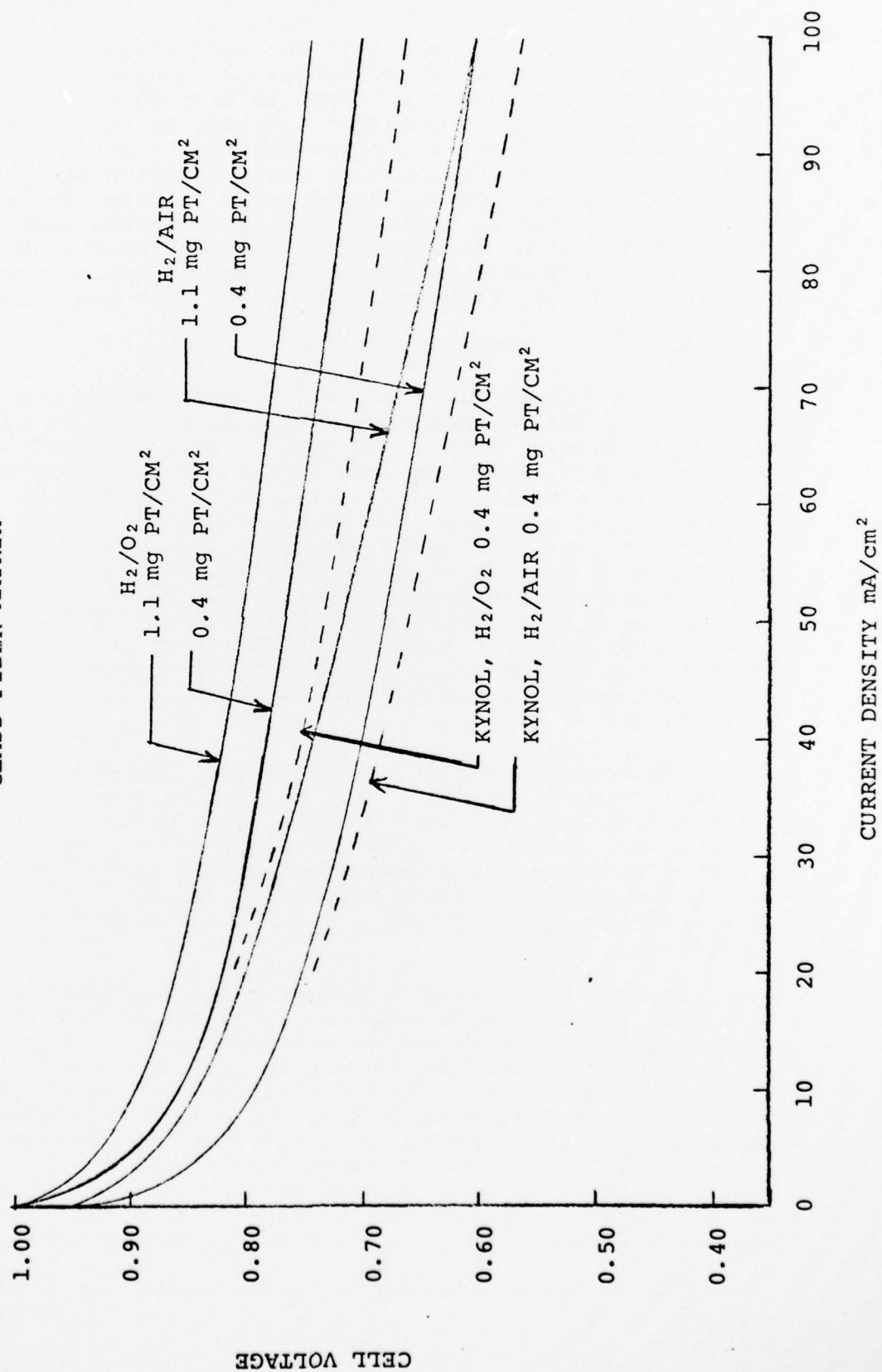


FIGURE 20

ULTRAMICRON TUNGSTEN CARBIDE

H. C. STARCK CO., BERLIN

50% TFMSA - 70°C

ANODE - 150 mg WC/cm²
CATHODE 2 mg Pt/cm²
MATRIX SiC

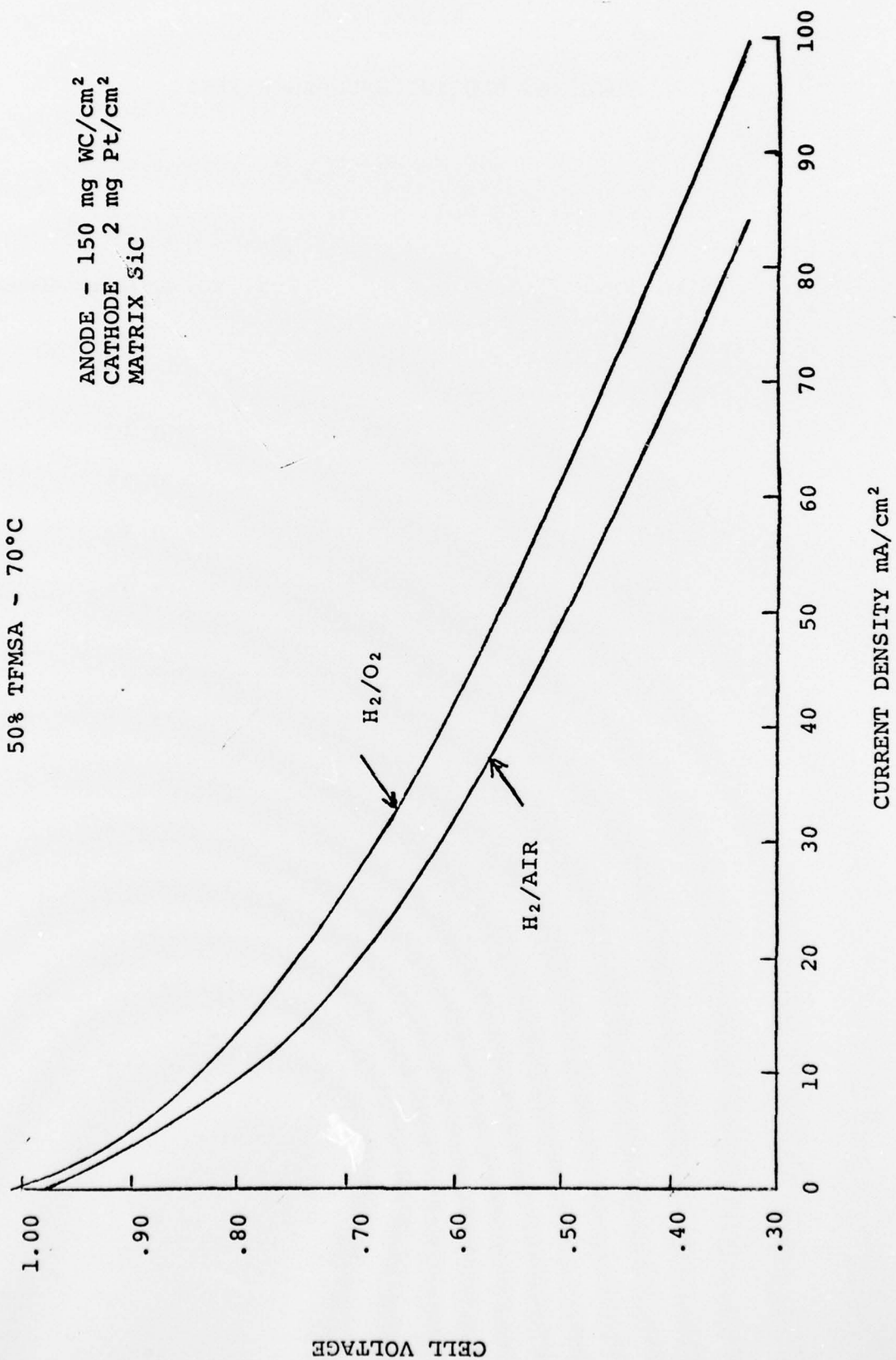


TABLE II

TUNGSTEN CARBIDE ENDURANCE TEST

150 mg WC/cm²

50 Vol. % TFMSA

Time, Hrs.	Cell Voltage at 40mA/cm ²
Initial	0.50
200	0.44
600	0.40
900	0.33
1300	0.30
1550	0.20

were made to expedite the activation procedure. Various activation techniques were evaluated. The most effective method appeared to be to anodically oxidize the WC in 30% KOH and 10% N_2H_4 at 70°C. This procedure was more effective in activating WC for use in sulfuric acid than for aqueous TFMSA. It was possible, however, to operate the activated WC anode initially in H_2SO_4 , thoroughly wash, and then reuse in a TFMSA cell with essentially equivalent anode polarization. Included in the data shown in Figure 21 is a comparison of the anode polarizations of H_2SO_4 and TFMSA cells. The anode polarizations were determined by driving a hydrogen consuming WC electrode versus a hydrogen evolution Pt black electrode and assuming the polarization for the evolution reaction was essentially nil. In Figure 21, there is also shown full cell polarization for both 50% TFMSA and H_2SO_4 cells. The results indicate a severe voltage penalty of about 380 mV at 100 mA/cm^2 when using the non noble metal anode catalyst. Further catalyst improvements are probably necessary to warrant its use in aqueous TFMSA cells.

Several other tungsten carbides were evaluated under this study. This included use of H. C. Starck HC-80, Sylvania Syl-Carb-105, and some experimental WC batches prepared by Stonehart Associates. Catalyst performances were generally inferior to the Starck Ultramicron WC, possibly due to low initial catalyst surface area.

5.0 SILICON CARBIDE

Specific development of a silicon carbide matrix was made an integral part of this investigation. It was recognized that any organic matrix material except for the fluorocarbons would be susceptible to some chemical degradation over long periods in the presence of TFMSA. Matrix degradation could not only lead to mixing of the reactant gases but also corrosion products from the matrix could be possible poisons for the fuel cell catalysts. During aqueous TFMSA cell endurance testing with the organic Kynol matrix, there was some evidence that cell decay was related to an anode poisoning effect, especially when low Pt loaded electrodes were utilized.

Fabrication of a discrete paper-like matrix of silicon carbide was viewed as easier to accomplish with a fibrous form rather than the particulate form. A process for producing a silicon carbide with average fiber lengths of about 50 microns has been developed utilizing rice hulls as the starting material.¹⁹ Experimental lots of this material are now available from Silag, Inc.

A procedure was developed for fabricating a paper-like composite structure of silicon carbide and PTFE utilizing a filtration process. The process required 15 weight percent of PTFE in a dispersion form to be added to the silicon carbide to give the composite adequate structural integrity. Matrices with thicknesses of approximately .020" and 80% porosities could be fabricated using this technique. Although wickability of the matrix

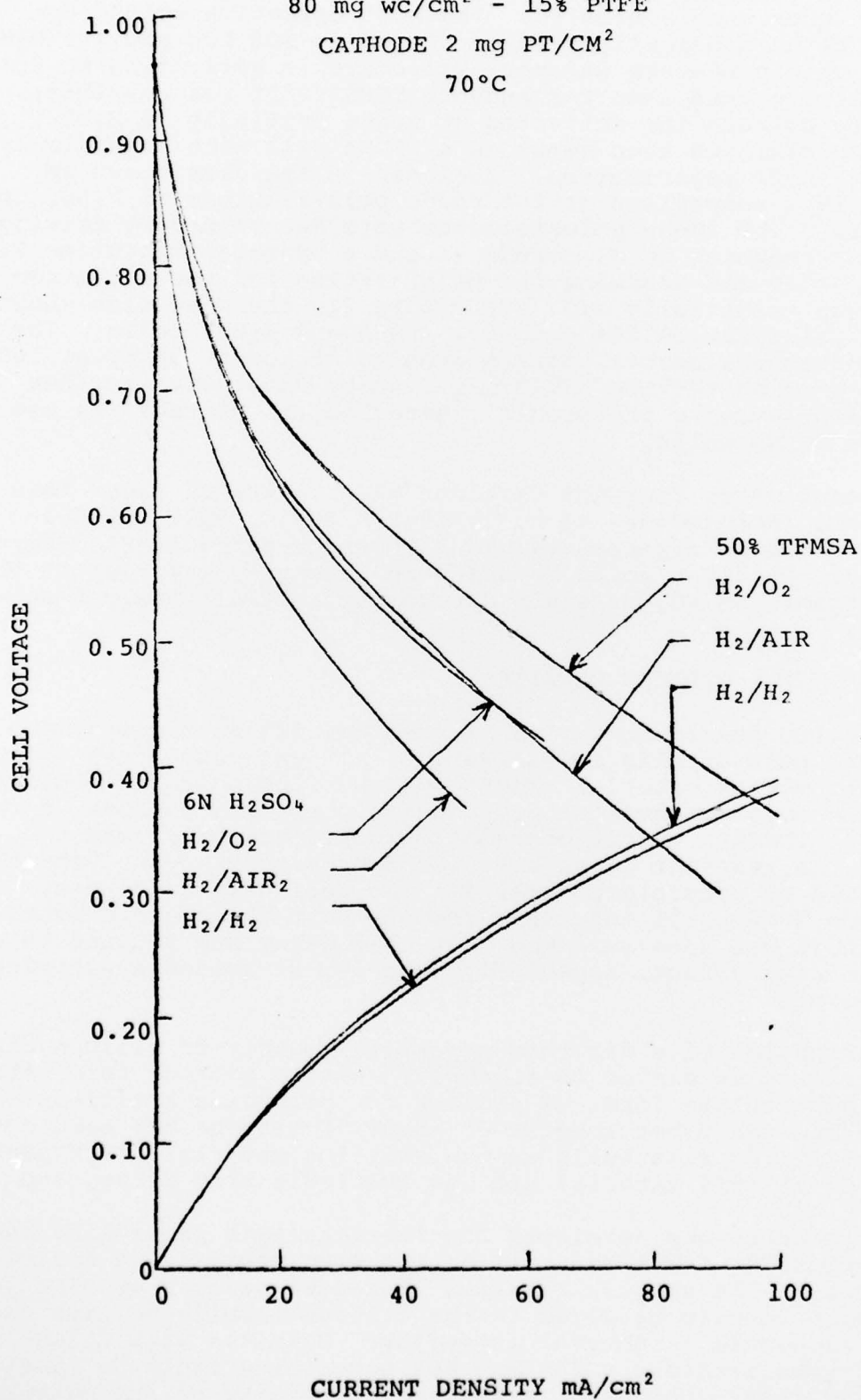
FIGURE 21

ULTRAMICRON TUNGSTEN CARBIDE

80 mg wc/cm^2 - 15% PTFE

CATHODE 2 mg PT/CM^2

70°C



was not optimum because of the relatively high PTFE contents, excellent fuel cell performances were generally attained with SiC-PTFE composite. As previously shown in Figure 9, the performance improvement with the SiC over a Kynol matrix has been typically 40 to 50 mv at 100 mA/cm².

Recently some difficulty has been experienced in receiving consistent batches of the fibrous silicon carbide from the supplier. Some batches have been marked by the presence of carbon or silicon dioxide leading to either conductivity or wetting problems of the resulting matrix structure. The potential of a silicon carbide matrix in conjunction with aqueous TFMSA electrolytes, however, has been shown. Further evaluation of different forms of silicon carbide and refinement of fabrication techniques is probably justified.

6.0 CONCLUSIONS

The use of TFMSA monohydrate as an electrolyte for a practical hydrogen-air fuel cell does not appear to be feasible due to volatility, conductivity, and wetting limitations. In particular, the monohydrate was shown to be volatile at temperatures in excess of 90°C; readily wetted PTFE the binder commonly utilized in porous fuel cell electrodes; and exhibited very poor ionic conductivity characteristics.

Aqueous TFMSA solutions ranging in concentrations from 25 to 60 volume percent were shown to be good ionic conductors and did not appear to wet PTFE as did the monohydrate. Very attractive hydrogen air fuel cell performance levels were exhibited by aqueous TFMSA cells at temperatures ranging from 23 to 70°C. At 70°C some indications were present that electrolyte decomposition might be occurring. At room temperature an endurance capability of over 2,000 hours was shown for dilute TFMSA cells with only a nominal performance loss. In addition, it was shown that low temperature cells could be operated for long periods without electrolyte replenishment and cell water balance could be maintained using high air flow rates. Generally, considerably higher performance was achieved than with any other acid electrolyte system equated under similar conditions.

Tungsten carbide was successfully operated as an hydrogen oxidation catalyst in aqueous TFMSA. The best anode polarization obtained in a fuel cell was 380 mV at 100 mA/cm². The endurance capability of the catalyst was limited, indicating that further improvements are necessary to make it attractive for use in a low temperature aqueous TFMSA fuel cell.

Aqueous TFMSA fuel cells with fibrous silicon carbide matrices were shown to give high initial performance levels. Silicon carbide is potentially a very attractive matrix material for use with TFMSA because of its stability. Further improvements are necessary to improve both its wettability and structural integrity.

7.0

RECOMMENDATIONS

Additional work is necessary for aqueous solutions of TFMSA. In particular, it is necessary to optimize supported catalyst type electrodes and matrix structures for long term stability. Also the exact temperature limitations of the electrolyte and various fuel cell components need to be determined. Since aqueous TFMSA fuel cells are restricted to low temperatures, it will be necessary to determine what carbon monoxide levels can be tolerated with various types of noble metal catalysts. More exact operating conditions for maintaining water balance must be determined and vapor pressure data for water over TFMSA should be obtained.

The very attractive fuel cell performance levels obtained with TFMSA under the program, in a relatively short time period, warrant further efforts be expanded to develop this system.

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